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The caesium oxygen interactions in the crystalline solids

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ABSTRACT

Through the study of the Cs–O bonds registered in the literature one observes that:

(i) the bond lengths range from 2.46 to 3.60 Å;
(ii) the preferential coordination numbers adopted by the caesium ions are 8, 9 and 10 but values from 1 to 12 also exist;
(iii) the average bond lengths increase with the coordination (CN) of the caesium ions with the following values: 2.714 Å (CN = 1), 2.98 Å (CN = 2), 3.057 Å (CN = 3), 3.104 Å (CN = 4), 3.149 Å (CN = 5), 3.188 Å (CN = 6), 3.224 Å (CN = 7), 3.245 Å (CN = 8), 3.261 Å (CN = 9), 3.269 Å (CN = 10), 3.293 Å (CN = 11) and 3.323 Å (CN = 12).

A new $R_{ij} = 2.469$ constant is determined with all the caesium coordination polyhedra to compute electrostatic bond valence sums.

The U_{eq} values of caesium in crystal structure are about 0.03 and generally less than 0.06 similar to those of the oxygen atoms and often bigger.

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1. Introduction

Contrary to the transition metals that have short ranges of bonding distances with oxygen atoms and present generally few coordination numbers, the alkaline ions show a large range of distances with oxygen atoms and a wide panel of coordination numbers.

Through the alkaline ions of the first column of the periodic table of the elements, caesium is that which raises the most controversy about the length of its bonds with oxygen atoms and also about its thermal motion factors in crystal structures.

So all the compounds containing caesium ions, only bonded to oxygen atoms, were collected through the ICDS data bank [1] in order to study first the Cs–O distances and their distribution, second the coordination of caesium, and third the thermal motion factors observed in the crystal structures and their comparison versus those of the corresponding oxygen atoms. For more reliability in the results only the structures solved from single-crystal X-rays diffraction with good *R* factors were used.

2. Results and discussion

To study the distribution of the Cs–O bond lengths one must first determine the longest interaction considered as a bond. To do that, a process described by Donnay and Allmann [2] was used. The ionic radii of caesium ions corresponding to different coordination numbers [3] are plotted versus the ideal bond valence "vi" which is defined as the quotient of the cationic charge by the coordination number. The maximum ionic radius is obtained by extrapolating the curve to the ideal bond valence vi = 0. The maximum Cs–O bond length 3.60 Å is computed by adding the maximum ionic radius (2.15 Å) of caesium deduced from the plot, to the maximum radius of oxygen (1.45 Å) [2].

Through the 1131 Cs ions registered, coordination numbers ranging from 1 to 12 were observed. Fig. 1a shows the distribution of these coordination numbers, which seems to be somewh at erratic. Note that there are about two times more even number of oxygen atoms (62.51%) than odd numbers (37.49%). Fig. 1b and c evidenced different and more regular behaviour when the number of oxygen bonded to caesium is odd or even. For the odd numbers one observes a slow regular increase of the number of polyhedra with the coordination number up to a sharp maximum (48.58%) for the nine apices polyhedron. For the even numbers the increase is quicker with a broad maximum including the eight (27.02%) and the 10 (32.25%) apices polyhedra. So caesium adopts mainly the coordination numbers 8, 9, 10, which

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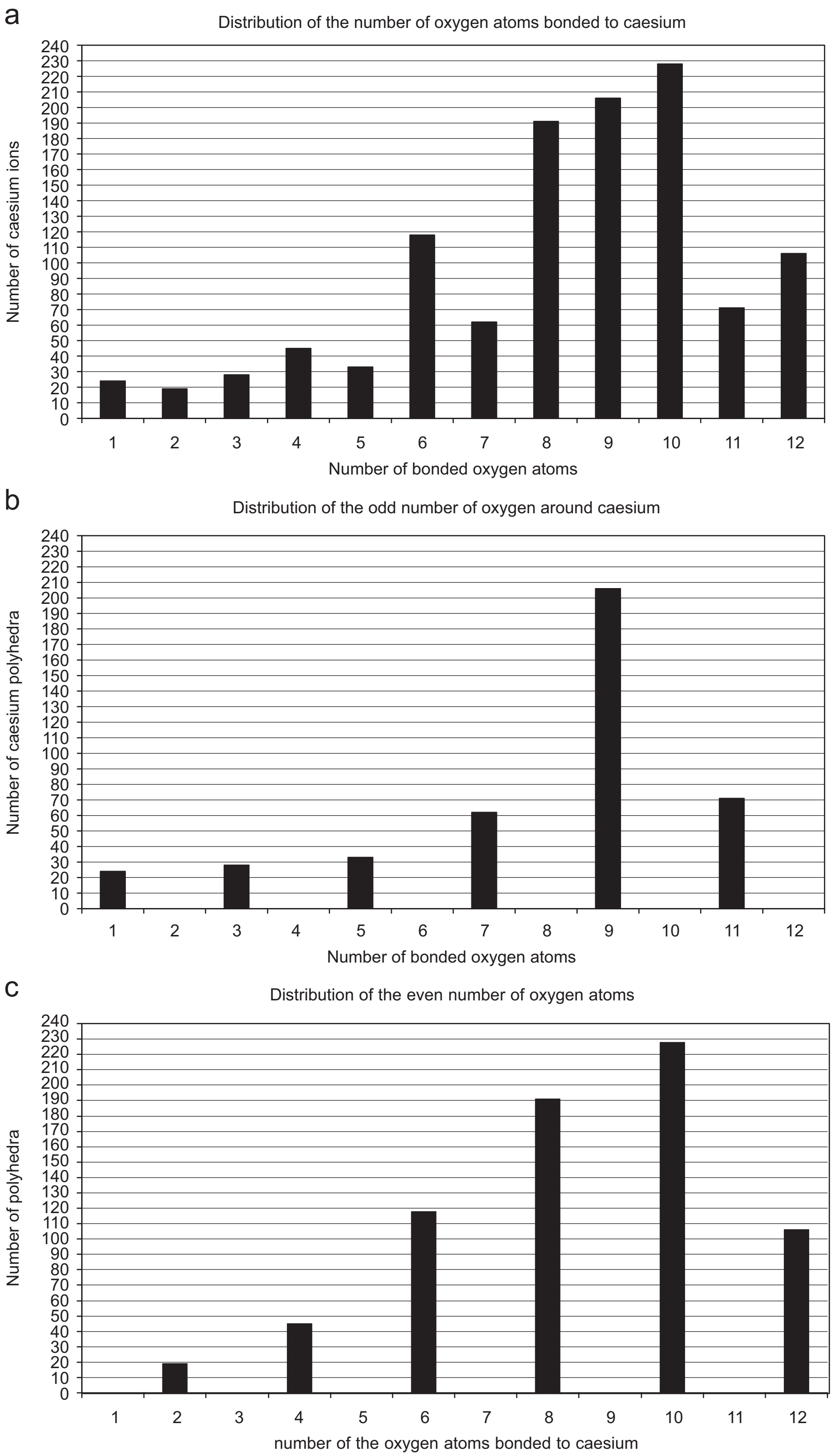

Fig. 1. Distribution of the coordination numbers of caesium ions with: (a) all the caesium ions registered, (b) the odd coordination numbers, and (c) the even coordination numbers.

represent about 55.26% of the observed coordination in the literature.

Table 1 resumes the average values and the median values of all the Cs–O distances, and those according to the coordination numbers, and according to the rank of the bonds in the polyhedra. The rank is defined by classing the Cs–O bonds of a polyhedron in increasing order of the bond length values, so the rank 1 corresponds to the shortest Cs–O bond in the

Table 1
Average and median values of the Cs–O distances in each polyhedron and in each rank

Coordination	Cs–O Average Median	(Cs–O) 1	(Cs–O) 2	(Cs–O) 3	(Cs–O) 4	(Cs–O) 5	(Cs–O) 6	(Cs–O) 7	(Cs–O) 8	(Cs–O) 9	(Cs–O) 10	(Cs–O) 11	(Cs–O) 12
1	2.714(13) 2.729	2.714(13) 2.729											
2	2.98(3) 2.923	2.95(4) 2.914	3.01(4) 2.941										
3	3.057(18) 2.986	2.99(3) 2.948	3.05(3) 2.979	3.12(3) 3.083									
4	3.104(15) 3.091	2.98(2) 2.970	3.03(2) 3.005	3.17(3) 3.172	3.24(3) 3.200								
5	3.149(15) 3.139	2.93(2) 2.908	3.06(2) 3.060	3.143(17) 3.139	3.24(2) 3.199	3.37(3) 3.348							
6	3.188(6) 3.180	3.065(16) 3.067	3.102(13) 3.102	3.153(11) 3.142	3.217(12) 3.225	3.276(13) 3.257	3.314(15) 3.283						
7	3.224(9) 3.215	2.998(15) 3.028	3.093(12) 3.091	3.147(11) 3.137	3.216(12) 3.209	3.285(13) 3.263	3.374(14) 3.345	3.453(14) 3.477					
8	3.245(5) 3.229	3.046(9) 3.049	3.102(8) 3.106	3.163(7) 3.158	3.200(7) 3.196	3.279(8) 3.264	3.321(8) 3.310	3.397(9) 3.393	3.455(9) 3.483				
9	3.261(4) 3.249	3.051(8) 3.060	3.105(7) 3.102	3.148(6) 3.151	3.214(6) 3.208	3.255(6) 3.251	3.296(6) 3.291	3.371(7) 3.373	3.433(7) 3.444	3.474(7) 3.506			
10	3.269(3) 3.263	3.060(6) 3.068	3.094(56) 3.103	3.165(5) 3.156	3.194(5) 3.187	3.244(5) 3.236	3.275(6) 3.269	3.352(5) 3.348	3.384(5) 3.392	3.438(5) 3.437	3.483(6) 3.506		
11	3.293(6) 3.281	3.056(10) 3.063	3.123(8) 3.121	3.159(9) 3.162	3.202(8) 3.198	3.239(9) 3.234	3.294(9) 3.270	3.326(9) 3.311	3.371(9) 3.358	3.420(8) 3.409	3.491(8) 3.491	3.543(6) 3.553	
12	3.323(5) 3.346	3.157(16) 3.134	3.173(15) 3.161	3.205(14) 3.214	3.213(14) 3.221	3.273(12) 3.266	3.279(12) 3.271	3.368(12) 3.370	3.375(12) 3.390	3.431(10) 3.456	3.444(10) 3.464	3.474(9) 3.484	3.480(9) 3.486
All	3.255(2) 3.247	3.044(4) 3.055	3.102(4) 3.104	3.161(3) 3.158	3.209(3) 3.204	3.266(3) 3.253	3.301(4) 3.291	3.373(4) 3.366	3.411(4) 3.417	3.447(4) 3.456	3.474(4) 3.485	3.502(6) 3.514	3.480(9) 3.486

The rank of a bond in a polyhedron is obtained by classing them in the increasing of their length.

polyhedron. As expected the average values of the Cs–O distances are increasing from 2.714 to 3.323 Å with the coordination numbers (Fig. 2a), and the same behaviour is observed with the median Cs–O distances (Fig. 2b). In the same kind of polyhedron the average values of the Cs–O bonds in each rank are also increasing with the order of the rank as seen, for example, in Fig. 3 for the 10-fold polyhedra which increase linearly from 3.060 to 3.482 Å.

One characteristic of the Cs–O bonds is the wide range of distances (Fig. 4), the shorter one indexed is 2.46 Å and the maximum determined by the Donnay and Allmann process is 3.60 Å, corresponding to a variation of about 1.14 Å. The strange feature of the distribution curve (Fig. 4) is principally due to the fact that it is the sum of several curves the size of which decreasing with the rank of the bonds. The curves corresponding to the rank 1–5, which contain more Cs–O bonds than the ranks 6–12, are more symmetrical and show also a more Gaussian feature.

These curves show also that a lot of Cs–O distances are less than 3 Å. Fig. 5 resumes the distribution of the Cs–O distances less than a given value. One observes in Fig. 5a corresponding to all the Cs–O bonds indexed that about 7% of these bonds are less than 3 Å. If one details the observations according to the rank of the bonds, one sees (Fig. 5b) that about 32% of the shortest bonds in a polyhedron (rank1) are less than 3 Å and 16% of the bonds of rank 2 and finally 5% of the bonds of rank 3. The bonds with a rank greater than 5 are all above 3 Å.

Through the bonds of the first rank, the rates of bond lengths shorter or equal to 3 Å decrease from 100% to 18% with the increase of the coordination of the caesium ions (Fig. 6).

The large range of Cs–O distances has an effect on the evaluation of the electrostatic bond valence sums received by the caesium ions. With the R_{ij} value of 2.42 quoted by Brese and O'Keeffe [4] the electrostatic bond valence sums range from 0.1 to 2.66 and Fig. 7a shows a broad distribution curve with a width at half height of about 0.4 valence-units. The fitting of the R_{ij} value to 2.469 by using all the caesium ions studied in the present paper leads to a similar curve with the same width but shifted (Fig. 7b). Unfortunately a large range of electrostatic bond valence sums (0.5–1.6) is observed for Cs ions and at first sight it seems that the results of the bond valence sums are not available to determine the valence received by the oxygen atoms in an inorganic compound. Let us consider the 10-fold coordinated caesium ions which are the most observed. The maximum bias is about 0.5 valence-units corresponding to a deviation of about 0.05 valence-units out of 2 for each bonded oxygen atom. This deviation is less than the error commonly observed on the oxygen bond valence, so one may consider that the results are reasonable particularly when the oxygen is mainly bonded to other kinds of atoms.

Caesium is, after Francium, the heaviest alkaline ion and many peremptory assertions are said about its thermal factor U_{eq} values in crystal structures. One of them is to claim that $U_{eq} \approx 0.005$ because the transition elements with similar Z present this kind of

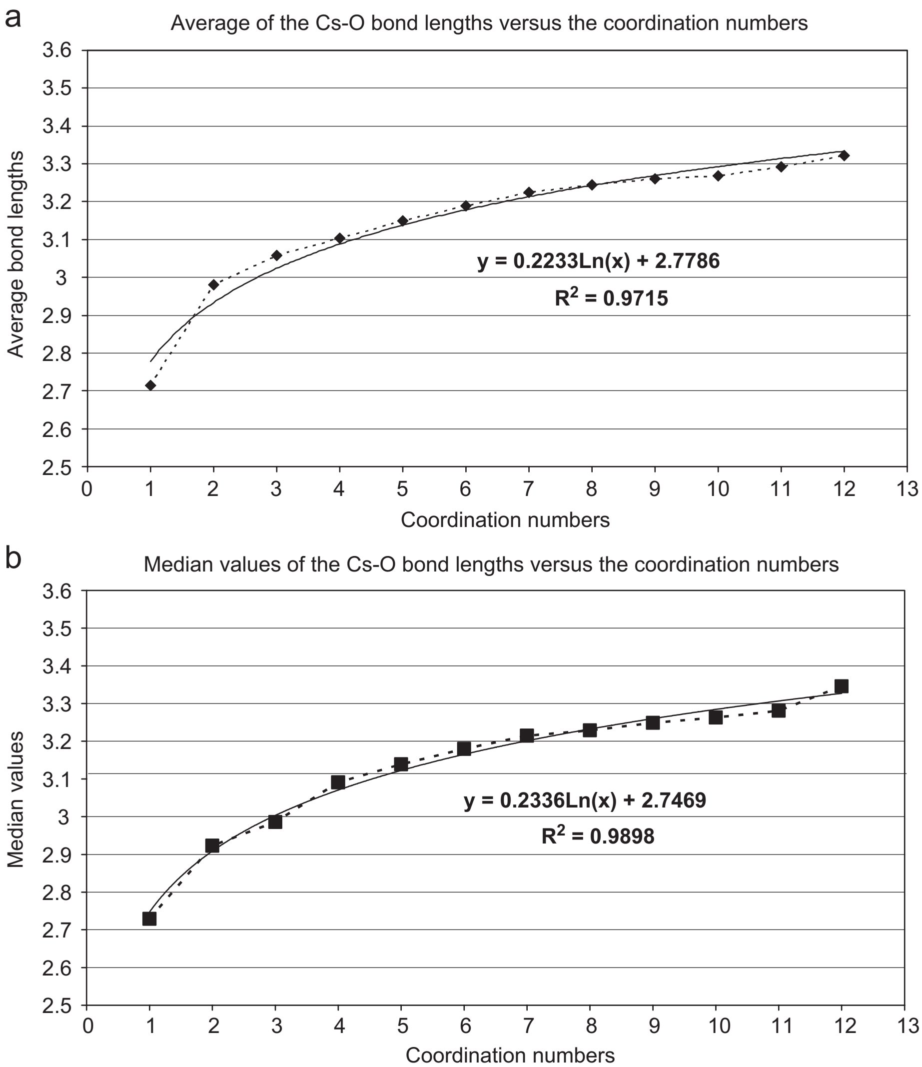

Fig. 2. (a) The average lengths of the Cs–O bonds in each kind of polyhedron. (b) The median values of the Cs–O bonds in each coordination number.

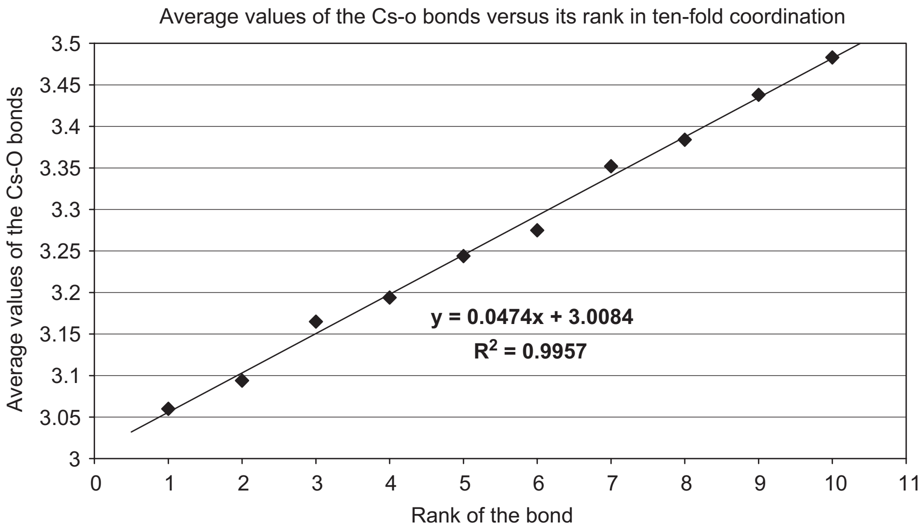

Fig. 3. The average values of the Cs–O bond lengths according to the rank of the bonds in the 10-fold coordination.

values. Another one is to claim that the U_{eq} value of the caesium ion must be lower than the U_{eq} values of the oxygen atoms of the crystal structure.

Fig. 8 shows that the U_{eq} values are about 0.03 and the most of them are less than 0.06. This demonstrates that the U_{eq} of caesium is greater than those of the corresponding transition elements, in

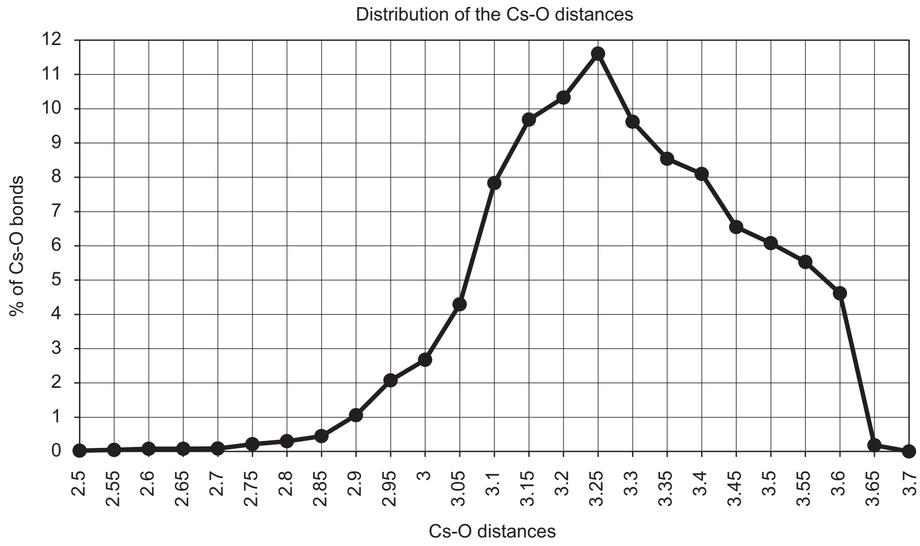

Fig. 4. The distribution of the Cs–O distances through all the caesium polyhedra.

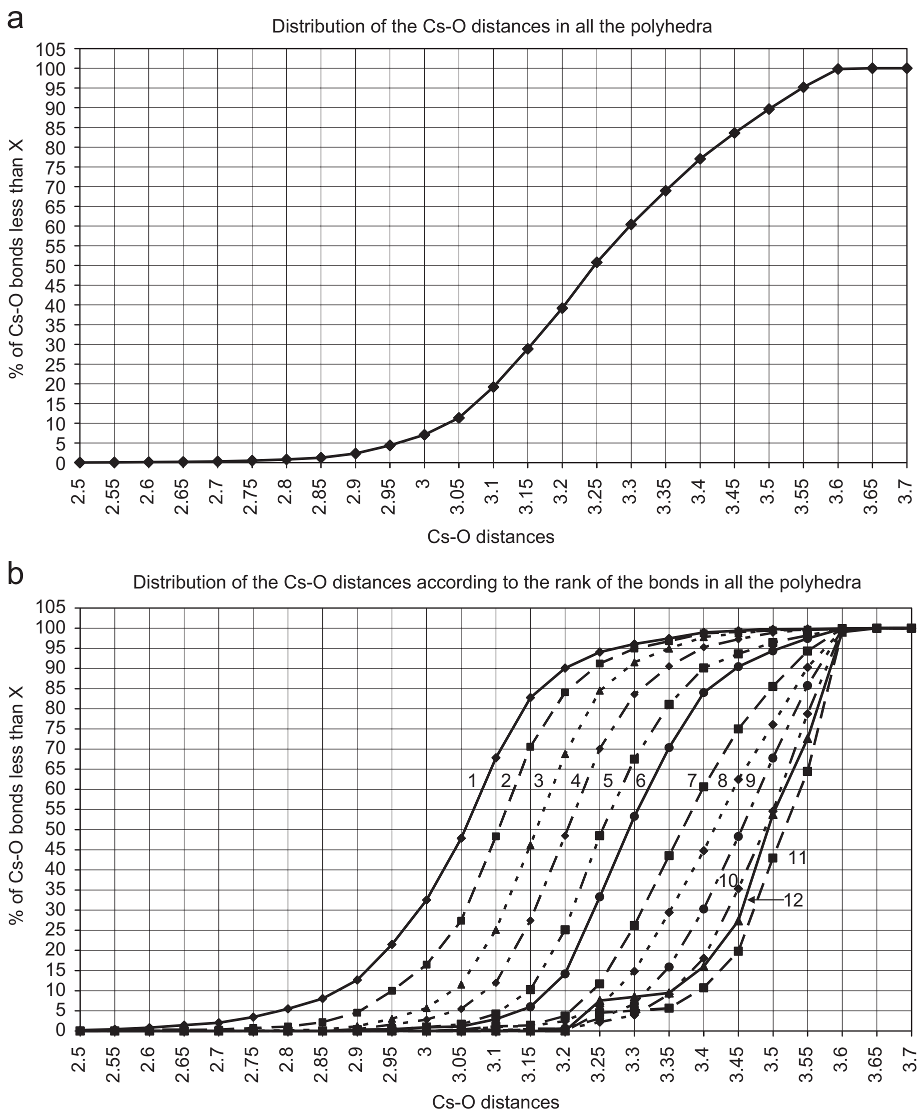

Fig. 5. The rate of Cs–O bonds less than a stated value: (a) with all the bonds (b) according to the rank of the bonds, pointed out by a number on the curves, in the polyhedra.

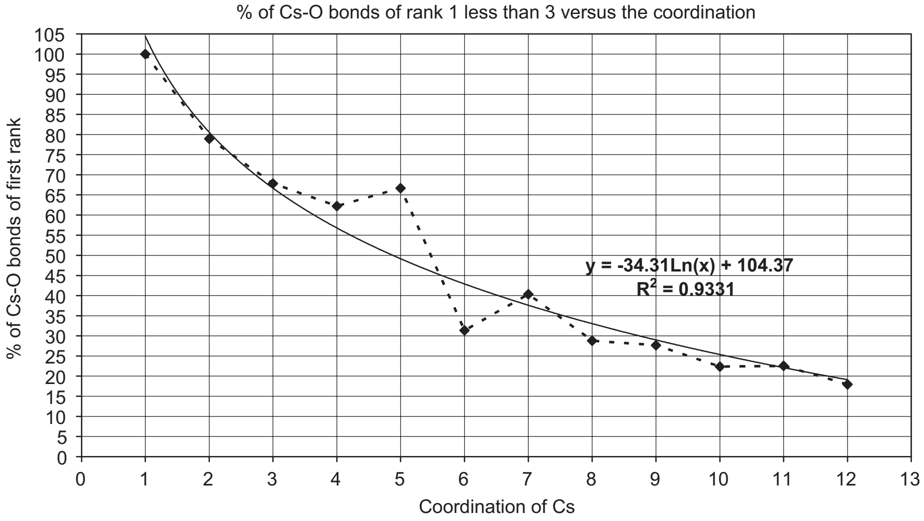

Fig. 6. The rate of Cs–O bonds of rank 1 less than 3 Å versus the coordination number of the Cs ions.

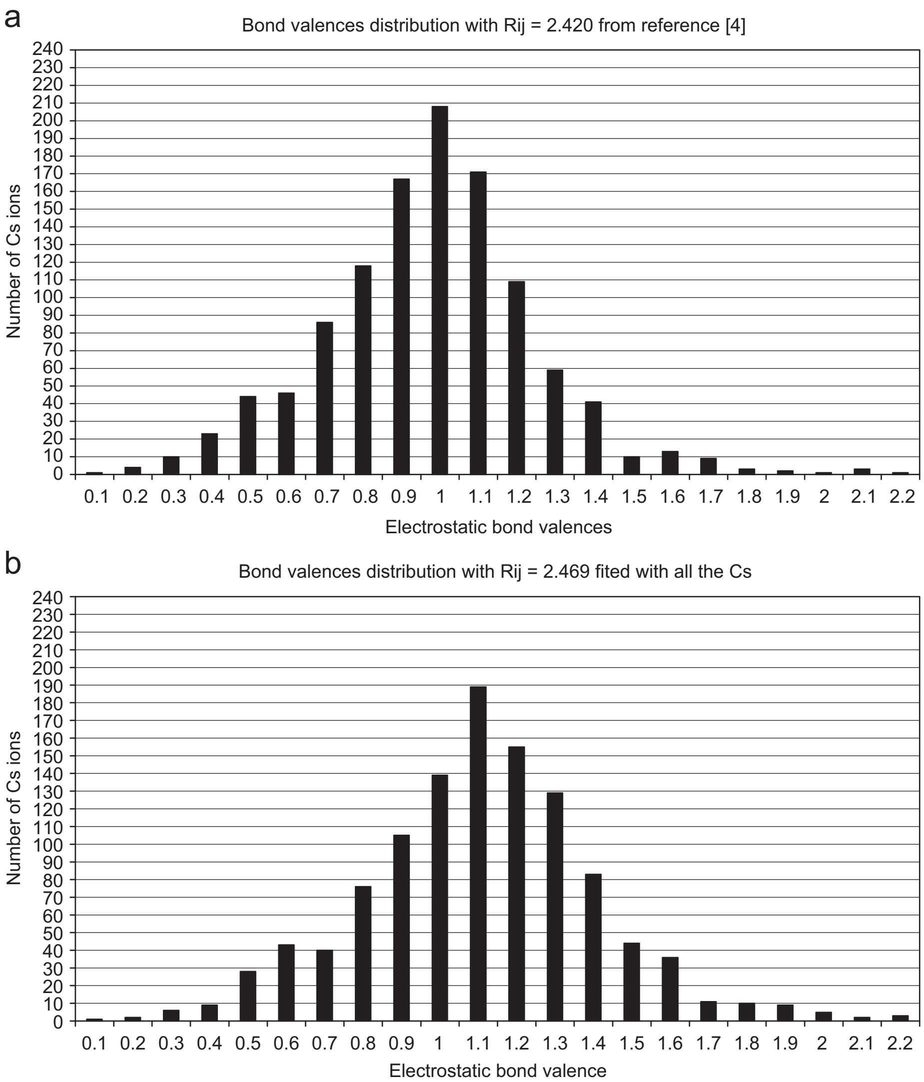

Fig. 7. The distribution of electrostatic bond valence sums calculated: (a) with the published $R_{ij} = 2.420$ [4] and (b) with $R_{ij} = 2.469$ fitted with all the registered Cs–O bonds.

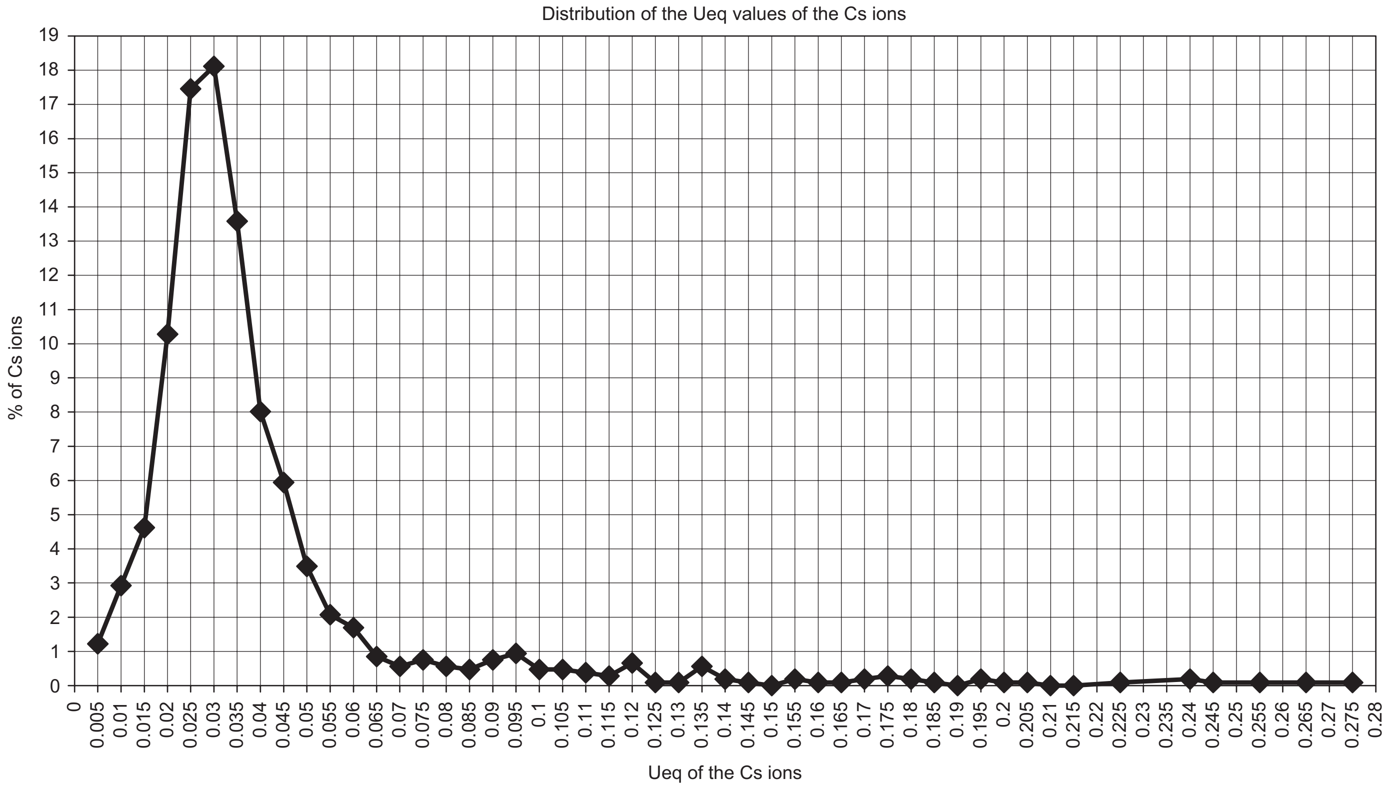

Fig. 8. Distribution of the thermal factors U_{eq} of the caesium ions in the crystal structure.

Table 2
Mean and median values of the U_{eq} of the Cs ions and of the ratio U_{eq} caesium/U_{eq} oxygen

Coordination	U_{eq} of Cs Average Median	$U_{eq}Cs/U_{eq}O_{av.}$	$U_{eq}Cs/U_{eq}O_{min}$	$U_{eq}Cs/U_{eq}O_{max}$
1	0.159(9)	1.79(11)	2.75(19)	1.44(14)
	0.1283	1.9023	2.6200	1.3860
2	0.088(14)	1.24(8)	1.60(16)	1.11(9)
	0.1020	1.1230	1.2823	1.0808
3	0.062(7)	1.6(3)	2.5(6)	1.1(2)
	0.0502	1.0624	1.6322	0.7723
4	0.035(5)	1.25(17)	1.6(3)	0.82(8)
	0.0277	0.9382	1.1186	0.6988
5	0.051(10)	1.7(3)	2.7(7)	0.97(12)
	0.0266	0.9747	1.1266	0.7743
6	0.037(3)	2.1(2)	3.3(4)	1.6(2)
	0.0283	1.5630	1.9866	1.0689
7	0.045(6)	1.71(12)	3.9(6)	0.96(6)
	0.0294	1.3809	2.0857	0.8286
8	0.0372(19)	2.03(18)	3.6(3)	1.49(18)
	0.0309	1.2842	1.9864	0.8750
9	0.0322(14)	1.45(14)	2.7(3)	1.02(13)
	0.0300	1.0051	1.5012	0.7608
10	0.034(3)	1.26(7)	2.12(15)	0.88(5)
	0.0267	0.9680	1.4533	0.7188
11	0.0239(12)	1.13(8)	2.4(3)	0.75(5)
	0.0222	1.0275	1.3061	0.7375
12	0.0295(19)	1.7(3)	2.2(3)	1.4(3)
	0.0252	1.1163	1.3612	0.9159
All	0.0381(12)	1.59(6)	2.82(14)	1.14(5)
	0.0285	1.1136	1.6056	0.8143

agreement with the fact that alkaline ions are generally sitting in the largest tunnels delimited by the crystal frameworks. Table 2 resumes the average values and the median values of the U_{eq} of caesium according to its coordination number. The high differences between the average values and the corresponding median values come from some very high U_{eq} up to 0.28 found in the literature as shown in Fig. 8 which bias the average values.

Concerning the comparison between the U_{eq} values of the caesium ions and the U_{eq} values of the oxygen atoms in a same crystal, every body knows that the refined U values include the thermal displacements of the atoms and also a part of the experimental errors, so to minimize this part the ratio $U_{eq}Cs/U_{eq}O$ of a structure were compared to those of other structure. As the thermal factors of the oxygen atoms are not equal in a same crystal, three kinds of ratios were used involving $U_{eq}O$ minimum, $U_{eq}O$ maximum and the average $U_{eq}O$.

The distribution curves in Fig. 9 show that the U_{eq} of the caesium ions is generally greater than the average of the oxygen U_{eq} values and even greater than the maximum U_{eq} of the oxygen atoms in the compounds.

The curves in Fig. 10 point out that about 80% of the Cs ions has a thermal factor $U_{eq}Cs$ greater or equal to the lowest oxygen thermal factor observed in the compound, and 40% of the Cs have a thermal factor twice the oxygen one. The same drawing shows that 58% of the Cs ions have thermal factors greater or equal to the average value of the thermal factors of the oxygen atoms in the compound. The ratio of Cs lowers to 32% if the comparison is made with the greatest oxygen thermal factor of the crystal.

3. Conclusion

The Donnay and Allmann [2] process allowed fixing at 3.60 Å the longest Cs–O bond, and the shortest bond length reported is 2.46 Å corresponding to a range of 1.14 Å.

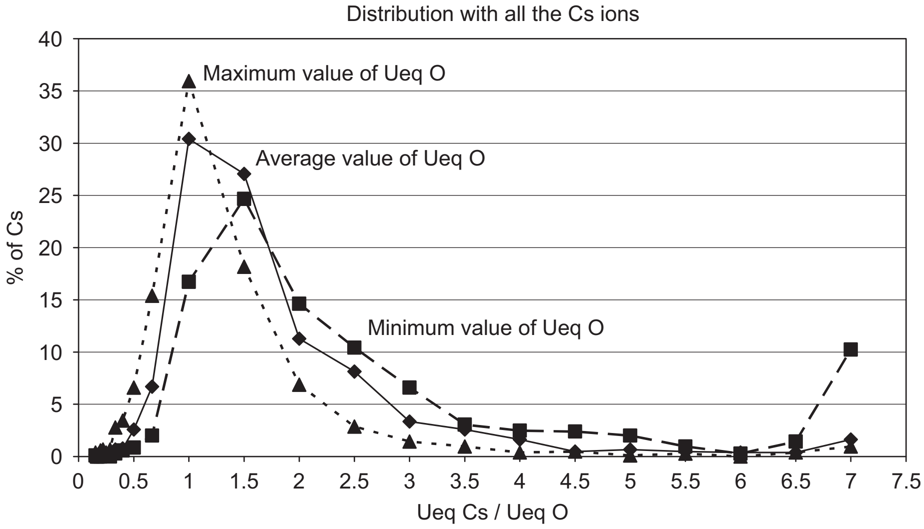

Fig. 9. Distribution of the $U_{eq}Cs/U_{eq}O$ values.

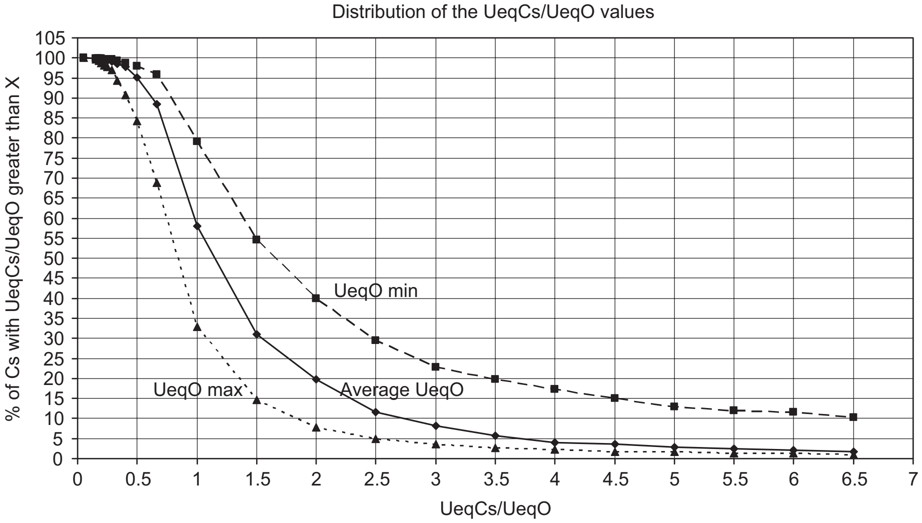

Fig. 10. Rate of $U_{eq}Cs/U_{eq}O$ greater than a stated value.

The caesium ions take up mainly the coordination numbers 8, 9 or 10.

The average Cs–O bond length increases from 2.714 Å to 3.323 Å with the coordination numbers.

About 32% of the shortest Cs–O bonds in a polyhedron (rank1) are less than 3 Å and 16% of the bonds of rank 2 and finally 5% of the bonds of rank 3. The bonds with a rank greater than 5 are all above 3 Å.

A new constant $R_{ij} = 2.469$ was determined with all the CsO_n polyhedra used in this study.

The equivalent thermal factors of the caesium ions in a crystal structure are generally of the same order or greater than those the oxygen atoms present in the crystal.

References

[1] Inorganic Crystal Structure Database, Fachinformationszentrum Karlsruhe, Germany.
[2] G. Donnay, R. Allmann, Am. Mineral. 55 (1970) 1003–1015.
[3] R.D. Shannon, Acta Crystallogr. A 32 (1976) 751–767.
[4] N.E. Brese, M. O'Keeffe, Acta Crystallogr. B 47 (1991) 192–197.