ON THE STRUCTURE OF TETRALEAD(II) COMPLEXES WITH OH BRIDGES

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In the memory of Professor Jozef Antalík (1945–2003).

Using Hartree–Fock, B3LYP and MP2 treatments, the optimal geometries and corresponding electronic structures of tetrahedral $[Pb_4(\mu_3\text{-}OH)_n]^q$ and $[Pb_4O(\mu_3\text{-}OH)_n]^{q-2}$ complex cations with total charges $q = 8 - n$, $n = 2, 3, 4$, are investigated. After OH^- removal, the central oxygen atom in $[Pb_4O(\mu_3\text{-}OH)_4]^{2+}$ is shifted to the apical position in $[Pb_4O(\mu_3\text{-}OH)_3]^{3+}$ whereas the $[Pb_4(\mu_3\text{-}OH)_2]^{6+}$ and $[Pb_4O(\mu_3\text{-}OH)_2]^{4+}$ complex cations are unstable. Direct Pb–Pb and O–O interactions are weakly antibonding in all the systems under study. The clusters are held together exclusively by relatively weak Pb–O bonds. A higher stability of the complex cations with a larger number of OH^- bridges may be confirmed.

Keywords: Lead(II) clusters; Hydroxo complexes; Molecular structure; Geometry optimizations; Ab initio calculations; DFT.

The structural characterization of lead compounds is important for understanding the mechanism of lead transport in natural systems. Discrete $[Pb(II)_x(O,OH)_y]^{n+}$ units containing 1, 2, 3, 4, 6, 7, 8 and 13 Pb atoms are known in real systems[1]. In aqueous solutions, $[Pb(OH)]^+$, $[Pb_3(OH)_4]^{2+}$, $[Pb_3(OH)_5]^+$, $[Pb_4(OH)_4]^{4+}$ and $[Pb_6(OH)_8]^{4+}$ clusters have been identified[2]. The species $[Pb(OH)]^+$, $[Pb_2(OH)_3]^+$ and $[Pb_2(OH)_2]^{2+}$ have been detected in melts[3]. A cluster containing three Pb atoms has not been found yet in crystalline salts[1], although the $[Pb_7O(OH)_3]^{9+}$ cluster[4] can be visualized as a central $[Pb_3O(OH)_3]^+$ cluster surrounded by four Pb atoms. A simple $[Pb_2(OH)]^{3+}$ unit[5] occurs in $Na[Pb_2(OH)](CO_3)_2$ and a disordered $[Pb_2(OH)(H_2O)_3]^{3+}$ cluster in lead hydrosodalite[6], $[Pb_2(OH)(H_2O)_3]_2[Al_3Si_3O_{12}]_2$.

A $[Pb_4(OH)_4]^{4+}$ cluster occupies the sodalite cage[7] in zeolite X and is present in maricopaite[8], $(Pb_7Ca_2)[Al_{12}Si_{36}(O,OH)_{100}]\cdot z(H_2O,OH)$, $z \approx 32$, in $[Pb_4(OH)_4](NO_3)_4$ [9], $[Pb_4(OH)_4]_3(CO_3)(ClO_4)_{10}\cdot 6H_2O$ [10] and $[Pb_4(OH)_4]$-

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$(ClO_4)_4 \cdot 2H_2O$ [11]. "Electrically neutral" $[Pb_4O_4]$ units are in the structure of aluminate sodalites[12] $Ln_4[Al_{12}O_{24}](Pb_4O_4)_2$ (Ln = Nd, Sm); they cannot be considered as independent clusters, since their O atoms are also closely bonded to Nd atoms to form OPb_3Ln tetrahedra linked in a three-dimensional framework[13]. Isolated $[Pb_4O]$ tetrahedra were found in $Pb_4O[Pb_2(BO_3)_3Cl]$ [14], $Pb_8Bi_2(PO_4)_6O_2$ [15] and $Pb_6Re_6O_{19}$ [16].

Clusters with composition $[Pb_6O(OH)_6]$ were found in both polymorphs of $[Pb_6O(OH)_6](ClO_4)_4 \cdot H_2O$ [17] and in $[Pb_6O(OH)_6](ReO_4)_4 \cdot H_2O$ [18]. The six Pb atoms in $[Pb_6O(OH)_6]^{4+}$ occupy the corners of three distorted Pb_4 tetrahedra connected by common faces. In $Pb_3O_2(OH)_2$, a topologically different $[Pb_6O_4(OH)_4]$ cluster was found[19]; it can be described as an almost regular Pb_6 octahedron whose eight triangular faces are "topped" by O atoms or OH groups. Isolated $[Pb_6O_2]$ clusters[20] occur in Pb_3UO_6. A $[Pb_7O(OH)_3]^{9+}$ cluster is present in zeolite A [4] and in synthetic "plumbonacrite"[21], $Pb_5O(OH)_2(CO_3)$.

Many larger clusters can be conveniently described considering the presence of oxo-centered OPb_4 groups[1,13]: several OPb_4 tetrahedra share edges to form a polytetrahedral $[Pb_xO_y]^{n+}$ cluster. Some solid crystals obtained from alkaline lead(II) solutions contain infinite $[Pb_3O_2]$ double chains of exclusively oxo-centered OPb_4 tetrahedra. These chains may be bonded by μ_2-OH bridges (like in $[Pb_6O_4](OH)(NO_3)(CO_3)$ [22] and $[Pb_3O_2](OH)(NO_3)$ [23]) or are not interconnected (like in $[Pb_3O_2](CO_3)$ [24]). Similarly, the isolated $[Pb_{13}O_8(OH)_6]^{4+}$ cluster (built from six μ_2-OH bridges and eight OPb_4 tetrahedra sharing a common Pb vertex and three edges) is the principal unit[25] of $[Pb_{13}O_8(OH)_6](NO_3)_4$. This implies that the Pb_4 tetrahedra sharing two and more faces are not stabilized by "outside" μ_3-OH bridges and one of these bridges is converted to "inner" oxide anion.

It is supposed[26] that $[Pb(II)_x(O,OH)_y]^{n+}$ clusters are stabilized by partial Pb–Pb bonding induced by bridging oxide/hydroxide ions. This conception is used also in chemistry textbooks[27]. On the other hand, semiempirical quantum-chemical studies[28] of possible structures of lead(II) hydroxo complexes indicate that the individual Pb atoms are bonded only via OH bridges due to vanishing Pb–Pb bonds. The stability of individual isomers increases with the number of OH bridges. This picture has been confirmed by ab initio MP2 study on dilead hydroxo complexes (except the relative stability of isomers)[29]. Other MP2 studies are restricted only to the structure and vibrational spectra of $[Pb_4(OH)_4]^{4+}$ [30] and $[Pb_6O(OH)_6]^{4+}$ [31] clusters.

This short review[1,28] shows the importance of tetralead $[Pb(II)_4(O,OH)_y]^{n+}$ clusters for understanding the formation, structure and bonding of lead hydroxo/oxo compounds. The aim of this study is ab initio investigation of

stable geometries and corresponding electronic structures of tetrahedral tetralead(II) clusters with hydroxyl bridges and the role of the central oxygen atom. This might be helpful for understanding the mechanisms of their formation in aqueous solutions and subsequent crystallization in real solid systems.

CALCULATIONS

Using the Gaussian 94 program package[32], the optimal geometries of tetrahedral $[Pb_4(\mu_3\text{-}OH)_n]^q$ and $[Pb_4O(\mu_3\text{-}OH)_n]^{q-2}$ complex cations with total charges $q = 8 - n$, $n = 2, 3, 4$, are investigated within standard restricted Hartree–Fock, B3LYP and MP2 treatments[33,34] using standard accuracy parameters. Dunning's correlation consistent cc-pVDZ basis sets have been used for O and H atoms[35] whereas the LANL2DZ effective core potential and (3s,4p,1d)/[2s,3p,1d] basis set[36,37] with diffuse and polarization functions[37,38] have been used for Pb atoms. Electron structure parameters have been evaluated in terms of Mulliken population analysis (gross atomic charges, overlap populations).

RESULTS AND DISCUSSION

We started our study with geometry optimizations of tetrahedral $[Pb_4(\mu_3\text{-}OH)_4]^{4+}$ and $[Pb_4O(\mu_3\text{-}OH)_4]^{2+}$ complex cations (Figs 1 and 2) and continued by consecutive removal of μ_3-OH bridges. We have found the optimized structures of the $[Pb_4(\mu_3\text{-}OH)_3]^{5+}$ and $[Pb_4O(\mu_3\text{-}OH)_3]^{3+}$ complex cations obtained in this way (Figs 3 and 4) what indicates their stability. On the other hand, the $[Pb_4(\mu_3\text{-}OH)_2]^{6+}$ and $[Pb_4O(\mu_3\text{-}OH)_2]^{4+}$ ones split into two parts during the geometry optimization, i.e. they are unstable. Such a behavior may be explained by an insufficient number of μ_3-OH bridges to keep together all the lead atoms[28,29]. This is supported by pushing the μ_4-O atom out from the central position in $[Pb_4O(\mu_3\text{-}OH)_4]^{2+}$ (Fig. 2) after μ_3-OH bridge removal to the lateral μ_3-O position in $[Pb_4O(\mu_3\text{-}OH)_3]^{3+}$ (Fig. 4). Despite this being a rough approximation, a comparison of the total energies of the systems under study (Table I) indicates that the reaction equilibria

$$[Pb_4(\mu_3\text{-}OH)_3]^{5+} + OH^- \rightarrow [Pb_4(\mu_3\text{-}OH)_4]^{4+} \quad (1)$$

$$[Pb_4O(\mu_3\text{-}OH)_3]^{3+} + OH^- \rightarrow [Pb_4O(\mu_3\text{-}OH)_4]^{2+} \quad (2)$$

should be shifted to the right.

As expected, the optimum geometries of the stable systems under study correspond to the highest possible T_d ($[Pb_4(\mu_3\text{-}OH)_4]^{4+}$ and $[Pb_4O(\mu_3\text{-}OH)_4]^{2+}$) or C_{3v} ($[Pb_4(\mu_3\text{-}OH)_3]^{5+}$ and $[Pb_4O(\mu_3\text{-}OH)_4]^{2+}$) symmetry point groups (Figs 1–4 and Tables II and III). Interatomic distances in $[Pb_4(\mu_3\text{-}OH)_4]^{4+}$ are shorter than the results of Jensen's MP2 calculations (Pb–Pb of 4.01×10^{-10} m, Pb–O_H of 2.51×10^{-10} m, O_H–H of 1.00×10^{-10} m)[30] and are in very good agreement with the corresponding perchlorate (Pb–Pb of 3.86×10^{-10} m, Pb–O_H of 2.4×10^{-10} m)[2f] and nitrate (Pb–Pb of 3.785×10^{-10} m, Pb–O_H of 2.38×10^{-10} m)[2k] solution data. Comparison with solid-state data is not effective due to large deformations caused by solid-state effects (e.g. differences in Pb–Pb distances over 0.2×10^{-10} m within the same structure).

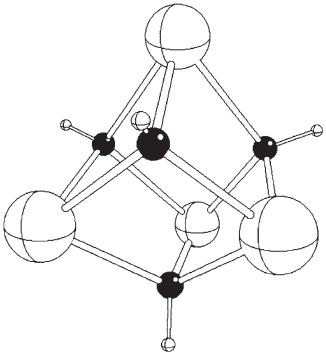

FIG. 1
Structure of $[Pb_4(\mu_3\text{-}OH)_4]^{4+}$

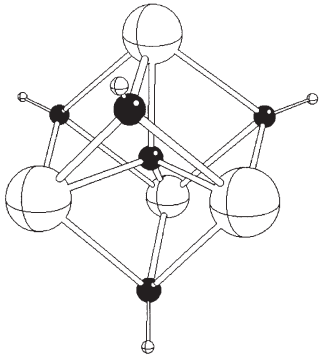

FIG. 2
Structure of $[Pb_4O(\mu_3\text{-}OH)_4]^{2+}$

According to the obtained results (Tables II and III), Pb–Pb and O_H–H distances are shorter in the complex cations with central O atom whereas Pb–O_H bond lengths show the opposite trend. On the other hand, Pb–Pb, Pb–O, Pb–O_H distances decrease and O_H–H bond lengths increase with the number of μ_3-OH bridges. These trends also determine the analogous bond angle trends.

The trends in positive lead and negative oxygen charges are implied by the total ion charges. The charge of (central) O atom is more negative and exhibits lower changes than those of the O_H ones. The positive H charge decreases with the number of O_H and O bridges. According to Mulliken bond orders, the character of Pb–Pb and O–O_H interactions is (weakly)

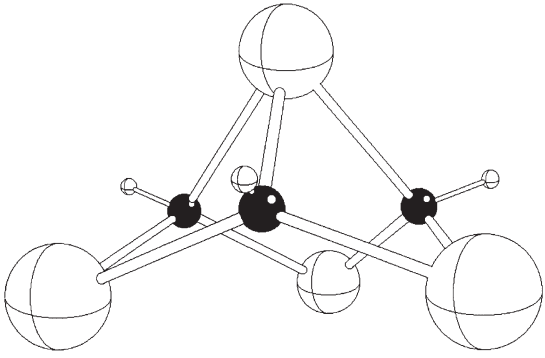

FIG. 3
Structure of $[Pb_4(\mu_3\text{-}OH)_3]^{5+}$

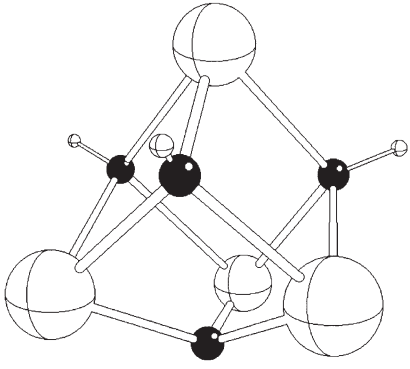

FIG. 4
Structure of $[Pb_4O(\mu_3\text{-}OH)_3]^{3+}$

antibonding. Thus they cannot stabilize the cluster as assumed in the literature[26,27]. Pb–O_H and Pb–O bonds are significantly weaker than the O–H ones. The Pb–O_H bond strength increases with the presence of central O, it is stronger than the Pb bond with O in central μ_4-position but weaker than with O in lateral μ_3-position.

Hartree–Fock, B3LYP and MP2 treatments exhibit similar trends. Unfortunately, recent Gaussian program packages can include solvent effects using various versions of Polarised Continuum Models based on dipoles (and higher multipoles) that are not suitable for charged systems[39]. Consequently, more sophisticated models of solvent effect are desirable for our studies.

Finally, higher stability of the complex cations with a larger number of OH^- bridges may be concluded in agreement with semiempirical AM1 treatment[28]. Stable tetralead hydroxo complexes must contain at least two μ_3-OH bridges otherwise they are destabilized due to Pb–Pb and O–O repulsion. The non-existence of $[Pb_4O(\mu_3\text{-}OH)_4]^{2+}$ complex cations in a real system may be explained by the structure of its $[Pb_4O(\mu_3\text{-}OH)_3]^{3+}$ intermediate (Fig. 4) with a lateral μ_3-O atom, which significantly increases the probability of the reaction (*3*)

$$[Pb_4O(\mu_3\text{-}OH)_3]^{3+} + H^+ \rightarrow [Pb_4(\mu_3\text{-}OH)_4]^{4+} \qquad (3)$$

TABLE I
Energy characteristics of the systems under study

Energy, a.u.	HF	B3LYP	MP2	HF	B3LYP	MP2
	no[a]	no[a]	no[a]	yes[a]	yes[a]	yes[a]
Total energy						
OH^-	–75.33086	–75.72143	–75.52566	–75.32242	–75.71389	–75.51758
$[Pb_4(\mu_3\text{-}OH)_4]^{4+}$	–313.88542	–315.87683	–314.86956	–313.82418	–315.81894	–314.81190
$[Pb_4O(\mu_3\text{-}OH)_4]^{2+}$	–389.75653	–392.20954	–390.98056	–389.69320	–392.15086	–390.92146
$[Pb_4(\mu_3\text{-}OH)_3]^{5+}$	–237.63763	–239.14770	–238.38539	–237.59287	–239.10584	–238.34311
$[Pb_4O(\mu_3\text{-}OH)_3]^{3+}$	–313.96819	–315.91779	–314.94913	–313.91854	–315.87159	–314.90241
Reaction energy						
Reaction (*1*)	–0.91693	–1.0077	–0.95851	–0.90889	–0.99921	–0.95121
Reaction (*2*)	–0.45748	–0.57032	–0.50577	–0.45224	–0.56538	–0.50147
Reaction (*3*)	0.08277	0.04096	0.07957	0.09436	0.05265	0.09051

[a] ZPE correction.

in comparison with reaction (*2*). Despite the $[Pb_4O(\mu_3\text{-}OH)_4]^{2+}$ complex cation seems to be bonded together stronger than the $[Pb_4(\mu_3\text{-}OH)_4]^{4+}$ one (see Table II for Pb–Pb distances), the energy data (Table I) indicate that its formation by reaction (*2*) is less advantageous in comparison with reaction (*1*). This statement is supported by expected higher stabilizing solvent effects of cations with higher charges in polar solvents. The existence of larger structures containing oxo-centered OPb_4 tetrahedra may be explained by the reactions of very reactive monolead(II) or dilead(II) hydroxo complexes[29]

TABLE II
Selected characteristics of $[Pb_4(\mu_3\text{-}OH)_4]^{4+}$ and $[Pb_4O(\mu_3\text{-}OH)_4]^{2+}$ cations

Characteristics	$[Pb_4(\mu_3\text{-}OH)_4]^{4+}$			$[Pb_4O(\mu_3\text{-}OH)_4]^{2+}$		
	HF	B3LYP	MP2	HF	B3LYP	MP2
Distances, 10^{-10} m						
Pb–O_H[a]	2.413	2.436	2.419	2.523	2.556	2.532
Pb–O	–	–	–	2.094	2.120	2.115
Pb–Pb	3.858	3.888	3.870	3.420	3.462	3.454
O–O_H[a]	–	–	–	2.268	2.299	2.265
O_H–H[a]	0.963	0.982	0.987	0.953	0.974	0.978
Angles, °						
Pb–O_H–Pb[a]	106.2	105.9	106.2	85.3	85.3	86.0
Pb–O–Pb	–	–	–	109.5	109.5	109.5
Pb–O_H–H[a]	112.6	112.9	112.5	128.5	128.5	128.1
O_H–Pb–O_H[a]	71.0	71.3	70.8	94.5	94.5	93.9
O–Pb–O_H[a]	–	–	–	58.0	58.0	57.5
Charges						
Pb	1.544	1.436	1.395	1.384	1.238	1.161
O_H[a]	–0.826	–0.860	–0.676	–0.774	–0.814	–0.618
O	–	–	–	–1.279	–1.103	–1.007
H	0.282	0.424	0.282	0.210	0.352	0.208
Bond orders						
Pb–O_H[a]	0.046	0.040	0.068	0.060	0.058	0.077
Pb–O	–	–	–	0.043	0.039	0.069
Pb–Pb	–0.032	–0.038	–0.030	–0.041	–0.048	–0.041
O_H–H[a]	0.344	0.309	0.315	0.349	0.314	0.311
O–O_H[a]	–	–	–	–0.079	–0.092	–0.071

[a] O_H denotes OH^- oxygen atoms (Figs 1 and 2).

TABLE III
Selected characteristics of $[Pb_4(\mu_3\text{-}OH)_3]^{5+}$ and $[Pb_4O(\mu_3\text{-}OH)_3]^{3+}$ cations

Characteristics	$[Pb_4(\mu_3\text{-}OH)_3]^{5+}$			$[Pb_4O(\mu_3\text{-}OH)_3]^{3+}$		
	HF	B3LYP	MP2	HF	B3LYP	MP2
Distances, 10^{-10} m						
Pb_{ax}–O_H[a]	2.446	2.475	2.475	2.329	2.343	2.344
Pb–O_H[a]	2.622	2.614	2.597	2.451	2.461	2.456
Pb_{ax}–O[a]	–	–	–	3.788	3.816	3.834
Pb–O	–	–	–	2.137	2.161	2.173
Pb_{ax}–Pb[a]	3.925	3.935	3.932	3.808	3.812	3.819
Pb–Pb	4.851	4.843	4.807	3.561	3.587	3.602
O–O_H[a]	–	–	–	2.709	2.744	2.742
O_H–H[a]	0.960	0.984	0.988	0.956	0.979	0.982
Angles, °						
Pb_{ax}–O_H–Pb[a]	101.5	101.2	101.6	105.6	105.0	105.4
Pb–O_H–Pb[a]	135.5	135.6	135.5	93.2	93.6	94.3
Pb_{ax}–O–Pb[a]	–	–	–	74.2	73.4	73.1
Pb–O–Pb	–	–	–	112.9	112.2	111.9
Pb_{ax}–O_H–H[a]	113.9	113.7	113.5	114.0	114.1	113.5
Pb–O_H–H[a]	102.4	102.5	102.3	117.8	118.1	117.9
O_H–Pb_{ax}–O_H[a]	72.2	71.6	70.9	75.8	76.4	75.7
O_H–Pb–O_H[a]	66.8	67.4	67.1	71.4	72.2	71.7
O–Pb_{ax}–O_H[a]	–	–	–	45.2	45.6	45.1
O–Pb–O_H[a]	–	–	–	72.0	72.5	72.3
Charges						
Pb_{ax}[a]	1.634	1.451	1.507	1.556	1.334	1.402
Pb	1.752	1.611	1.654	1.550	1.329	1.381
O_H[a]	–1.058	–0.845	–0.913	–1.071	–0.853	–0.927
O	–	–	–	–1.278	–0.974	–1.016
H	0.428	0.417	0.423	0.428	0.404	0.417
Bond orders						
Pb_{ax}–O_H[a]	0.015	0.046	0.039	0.016	0.055	0.047
Pb–O_H[a]	0.017	0.048	0.041	0.007	0.037	0.027
Pb_{ax}–O[a]	–	–	–	0.001	0.001	0.000
Pb–O	–	–	–	0.054	0.098	0.099
Pb_{ax}–Pb[a]	–0.044	–0.048	–0.040	–0.030	–0.035	–0.027
Pb–Pb	–0.018	–0.020	–0.017	–0.041	–0.058	–0.037
O_H–H[a]	0.320	0.303	0.291	0.327	0.310	0.298
O–O_H[a]	–	–	–	–0.032	–0.025	–0.028

[a] O_H denotes OH^- oxygen atoms and Pb_{ax} the axial lead atom, respectively (Figs 3 and 4).

with the above-mentioned tetralead(II) complex cations with oxo/hydroxo bridges. Nevertheless, more detailed experimental as well as theoretical studies in this field are desirable.

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REFERENCES AND NOTES

1. Kolitsch U., Tillmanns E.: *Mineral. Mag.* **2003**, *67*, 79; and the references therein.
2. a) Olin A.: *Acta Chem. Scand.* **1960**, *14*, 126; b) Olin A.: *Acta Chem. Scand.* **1960**, *14*, 814; c) Pajdowski L., Olin A.: *Acta Chem. Scand.* **1962**, *16*, 983; d) Hugel R.: *Bull. Soc. Chim. Fr.* **1964**, 1462; e) Hugel R.: *Bull. Soc. Chim. Fr.* **1965**, 968; f) Johansson G., Olin A.: *Acta Chem. Scand.* **1968**, *22*, 3197; g) Gyunner E. A., Tsareva A. I., Bakina N. B., Velmozhnyi I. S.: *Ukr. Khim. Zh.* **1978**, *44*, 348; h) Sylva R. N., Brown P. L.: *J. Chem. Soc., Dalton Trans.* **1980**, 1577; i) Cruywagen J. J., van de Water R. F.: *Talanta* **1993**, *40*, 1091; j) Arbatskii A. P., Benson V. V., Bolshakova E. V.: *Russ. J. Phys. Chem.* **1995**, *69*, 1730; k) Grimes S. M., Johnston S. R., Abrahams I.: *J. Chem. Soc., Dalton Trans.* **1995**, 2081.
3. a) Bengtsson L., Holmberg B.: *J. Chem. Soc., Faraday Trans.* **1990**, *86*, 351; b) Frostemark F., Bengtsson L. A., Holmberg B.: *J. Chem. Soc., Faraday Trans.* **1994**, *90*, 2531.
4. Ronay C., Seff K.: *Zeolites* **1993**, *13*, 97.
5. Krivovichev S. V., Burns P. C.: *Mineral. Mag.* **2000**, *64*, 1077.
6. Eiden-Assmann S., Schneider A. M., Behrens P., Wiebcke M., Engelhardt G., Felsche J.: *Eur. J. Chem.* **2000**, *6*, 292.
7. Nardin G., Randaccio L., Zangrando E.: *Zeolites* **1995**, *15*, 684.
8. Rouse R. C., Peacor D. R.: *Am. Mineral.* **1994**, *79*, 175.
9. Grimes S. M., Johnston S. R., Abrahams I.: *J. Chem. Soc., Dalton Trans.* **1995**, 2081.
10. Hong S.-H., Olin A.: *Acta Chem. Scand.* **1973**, *27*, 2309.
11. Hong S.-H., Olin A.: *Acta Chem. Scand., Ser. A* **1974**, *28*, 233.
12. Werner J. P., Műller-Buschbaum H.: *Z. Naturforsch., B: Chem. Sci.* **1997**, *52*, 449.
13. Krivovichev S. V., Filatov S. K., Semenova T. F.: *Russ. Chem. Rev.* **1998**, *67*, 137.
14. Behm H.: *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1983**, *39*, 1317.
15. Moore E. P., Chen H. Y., Brixner L. H., Foris C. M.: *Mater. Res. Bull.* **1982**, *17*, 653.
16. Abakumov A. M., Shpanchenko R. V., Antipov E. V.: *Z. Anorg. Allg. Chem.* **1998**, *624*, 750.
17. a) Spiro T. G., Templeton D. H., Zalkin A.: *Inorg. Chem.* **1969**, *8*, 856; b) Olin A., Söderquist R.: *Acta Chem. Scand.* **1972**, *26*, 3505.
18. Haag-Bruhl C., Fuess H., Lightfoot P., Cheetham A. K.: *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1988**, *44*, 8.
19. Hill R. J.: *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1985**, *41*, 998.
20. Sterns M., Parise J. B., Howard C. J.: *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1986**, *42*, 1275.
21. a) Krivovichev S. V., Burns P. C.: *Mineral. Mag.* **2000**, *64*, 1069; b) Brooker M. H., Sunder S., Taylor P., Lopata V. J.: *Can. J. Chem.* **1983**, *61*, 494.
22. Li Y., Krivovichev S. V., Burns P. C.: *J. Solid State Chem.* **2000**, *153*, 365.

23. Krivovichev S. V., Li Y., Burns P. C.: *J. Solid State Chem.* **2001**, *158*, 78.
24. Krivovichev S. V., Burns P. C.: *Mineral. Mag.* **2000**, *64*, 1077.
25. Li Y., Krivovichev S. V., Burns P. C.: *J. Solid State Chem.* **2001**, *158*, 74.
26. Bengtsson L. A., Hoffmann R.: *J. Am. Chem. Soc.* **1993**, *15*, 2666.
27. a) Cotton F. A., Wilkinson G.: *Advanced Inorganic Chemistry*, 5th ed., p. 297. Wiley, New York 1998; b) Ondrejovič G., Boča R., Jóna E., Langfelderová H., Valigura D.: *Anorganická chémia*, p. 366. Alfa, Bratislava 1993.
28. a) Breza M., Manová A.: *Collect. Czech. Chem. Commun.* **1995**, *60*, 527; b) Breza M., Manová A.: *Polyhedron* **1999**, *18*, 2085; c) Breza M., Manová A.: *Collect. Czech. Chem. Commun.* **1999**, *64*, 1269; d) Breza M., Manová A.: *Collect. Czech. Chem. Commun.* **2002**, *67*, 219.
29. Breza M., Biskupič S.: *Collect. Czech. Chem. Commun.* **2003**, *68*, 2377.
30. Jensen J. O.: *J. Mol. Struct. (THEOCHEM)* **2002**, *587*, 111.
31. Jensen J. O.: *J. Mol. Struct. (THEOCHEM)* **2003**, *635*, 11.
32. Frisch M. J., Trucks G. W., Schlegel H. B., Gill P. M. W., Johnson B. G., Robb M. A., Cheeseman J. R., Keith T. A., Petersson G. A., Montgomery J. A., Raghavachari K., Al-Laham M. A., Zakrzewski V. G., Ortiz J. V., Foresman J. B., Cioslowski J., Stefanov B. B., Nanayakkara A., Challacombe M., Peng C. Y., Ayala P. Y., Chen W., Wong M. W., Andres J. L., Replogle E. S., Gomperts R., Martin R. L., Fox D. J., Binkley J. S., Defrees D. J., Baker J., Stewart J. P., Head-Gordon M., Gonzales C., Pople J. A.: *Gaussian 94*, Revision D.1. Gaussian Inc., Pittsburgh (PA) 1995.
33. Becke A. D.: *J. Chem. Phys.* **1993**, *98*, 5648.
34. Møller C., Plesset M. S.: *Phys. Rev.* **1934**, *46*, 618.
35. Woon D. E., Dunning T. H., Jr.: *J. Chem. Phys.* **1993**, *98*, 1358.
36. Hay P. J., Wadt W. R.: *J. Chem. Phys.* **1985**, *82*, 299.
37. Basis sets were obtained from the Extensible Computational Chemistry Environment Basis Set Database, Version 2/12/03, Molecular Science Computing Facility, Environmental and Molecular Sciences Laboratory which is part of the Pacific NorthWest Laboratory, P.O. Box 999, Richland, Washington 99352, U.S.A. http://www.emsl.pnl.gov/forms/basisform.html
38. Check C. E., Faust T. O., Bailey J. M., Wright B. J., Gilbert T. M., Sunderlin L. S.: *J. Phys. Chem. A* **2001**, 105, 8111.
39. Buckingham A. D.: *Adv. Chem. Phys.* **1967**, *12*, 107.