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Ab Initio Calculations of Hydroxoplatinum Compounds: I. Hexahydroxoplatinum(IV), (V), and (VI) Complexes

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Abstract—The structural and spectral data on $\text{Pt}(\text{OH})_6^n$ clusters ($n = -2, -1, 0$) obtained by ab initio methods have been considered. The data for $n = -2$ are in good agreement with the published data on hexahydroxoplatinates(IV).

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Previously [1, 2], it was shown that oxidative synthesis in alkaline solutions of Pt(IV) leads to different dioxygen compounds containing the superoxo ligand (O_2^-). The structure of such compounds, existing primarily in solution, was confirmed by different physicochemical methods [3, 4], which are not direct structural methods and are therefore only indirect evidence of the assumed structure.

To examine the structural and spectral features of binuclear platinum(IV) superoxo complexes, we performed full geometry optimization and calculated vibrational spectra by ab initio methods. Inasmuch as the $\text{Pt}(\text{OH})_6^{n-}$ ions are the structural units of the binuclear superoxo complexes in question, we also calculated $\text{Pt}(\text{OH})_6^{n-}$ complexes, some of which have been structurally characterized [5].

COMPUTATIONAL DETAILS

The full geometry optimization of the complexes was performed at the Hartree–Fock level of theory with the GAMESS [6] and PC GAMESS [7] programs by the quasi-Newton–Raphson gradient method. Quasi-relativistic [8, 9] pseudopotentials of platinum describing 30 core atomic orbitals (AOs) were used in the calculations. In combination with pseudopotentials, $(8s7p6d)/(6s5p3d)$ contracted basis sets were taken. For O atoms, the quasirelativistic pseudopotential of the 1s inner shell with the $(4s5p)/(2s3p)$ basis set was used [8]. Closed-shell compounds were calculated by the restricted Hartree–Fock method. Open-shell structures were optimized by the unrestricted Hartree–Fock

method. The initial Fockian matrix elements were determined by the Huckel method.

The difference in electron density between two iterations was used as a criterion of convergence of the iteration process for the self-consistency procedure; for convergence, this difference should be no more than 10^{-7} au. For the geometric optimization, the total energy gradient of the system was taken as a criterion of convergence: the process was terminated when the maximal gradient was no more than 10^{-4} au. For the lowest energy clusters in each series, internal coordinates were refined, which decreased the error of calculation to 10^{-6} au. After that, vibrational spectra were calculated and analyzed.

To determine the normal mode frequencies, force constants were calculated by a numerical method. Small positive and negative displacements of atoms with an amplitude of 0.003 Bohr along each Cartesian coordinate were considered. The force constants were then transformed to a set of natural linearly independent internal coordinates.

The platinum–oxygen distance 1.95 Å [5, 10] was used as the initial one in the determination of the geometric parameters of clusters. To a first approximation, the oxygen–hydrogen distance was taken to be 1 Å. The initial HOPt angle was varied from 180° to 90°.

Calculations were performed for model fragments of composition $\text{Pt}(\text{OH})_6^n$ with $n = -2, -1, 0$, which corresponds to Pt(IV), Pt(V), or Pt(VI) complexes. Whereas both the geometric [5] and spectral [11] parameters are available for the first type of complex, analogous Pt(V) and Pt(VI) derivatives are unknown.

Table 1. Results of quantum-chemical calculations of hexahydroxoplatinum complexes $\text{Pt}(\text{OH})_6^n$

| Total charge of the cluster | Symmetry* | Pt–O distance, Å | PtOH angle, deg | Cluster energy, au |
|-----------------------------|----------------------|------------------|-----------------|--------------------|
| –2 | $C_{3i}(\mathbf{1})$ | 1.954 | 102.81 | –574.569 |
| | $C_{3i}(\mathbf{3})$ | 1.960 | 103.35 | –574.549 |
| | $C_{3i}(\mathbf{4})$ | 1.961 | 107.53 | –574.517 |
| | $C_{4h}(\mathbf{1})$ | 1.956 | 102.39 | –574.450 |
| –1 | | 1.920 | 180.00 | |
| | O_h | 1.918 | 180.00 | –574.202 |
| | C_i | 1.928 | 106.54 | –574.637 |
| | | 1.883 | 107.36 | |
| | | 1.883 | 107.38 | |
| | $C_{3i}(\mathbf{4})$ | 1.932 | 112.30 | –574.499 |
| | $C_{4h}(\mathbf{2})$ | 1.899 | 180.00 | –574.271 |
| | | 1.897 | 180.00 | |
| 0 | O_h | 1.454 | 180.00 | –570.553 |
| | C_i | 1.914 | 110.17 | –574.428 |
| | | 1.823 | 111.69 | |
| | | 1.823 | 111.70 | |
| | $C_{3i}(\mathbf{1})$ | 1.852 | 111.77 | –574.420 |
| | $C_{3i}(\mathbf{2})$ | 1.955 | 107.17 | –574.333 |
| | $C_{3i}(\mathbf{3})$ | 1.956 | 109.35 | –574.319 |
| | $C_{3i}(\mathbf{4})$ | 1.912 | 117.75 | –574.242 |
| | $C_{4h}(\mathbf{1})$ | 1.844 | 118.03 | –574.211 |
| | | 1.858 | 180.00 | |
| | $C_{4h}(\mathbf{2})$ | 1.790 | 180.00 | –574.133 |
| | | 1.864 | 180.00 | |

* Parenthesized is the number of a configuration as shown in Figs. 1 and 3.

Calculations were performed for clusters of different symmetry. The choice of the symmetry group was performed on the basis of the principle that higher symmetry groups contain lower symmetry groups (for example, $O_h \in O \in T_d \in T_h \in T$, $C_{3i} \supset C_3 \in C_i$, for the cases when the results of transformations and calculations for these symmetry groups are identical) and by other methods applicable to coordination compounds (the maximal ligand repulsion principle, the choice of symmetries corresponding to near-spherical geometries, etc.). This allowed us to exclude from consideration clusters with improbable geometries that corresponded to a minimum of the potential energy surface (PES) (these clusters can be exemplified by clusters

with symmetry of the C_{4v} type). Thus, the following point symmetry groups were considered in this work: O_h , C_{4h} , C_{3i} , and C_i . It is not necessary that each of these groups for each cluster correspond to a PES minimum. At the same time, for some symmetry groups (as a rule C_{3i}), the existence of several minima corresponding to different geometric structures of clusters turned out to be possible for the same object.

RESULTS AND DISCUSSION

The computation results obtained by geometry optimization of different platinum clusters are summarized in Table 1. As is seen, clusters of symmetry (C_{3i} (for $n = -2$) and C_i ($n = -1$ and 0) with very similar structures (Figs. 1–3) have minimal energies. For clusters

¹ $C_{3i} \equiv S_6$.

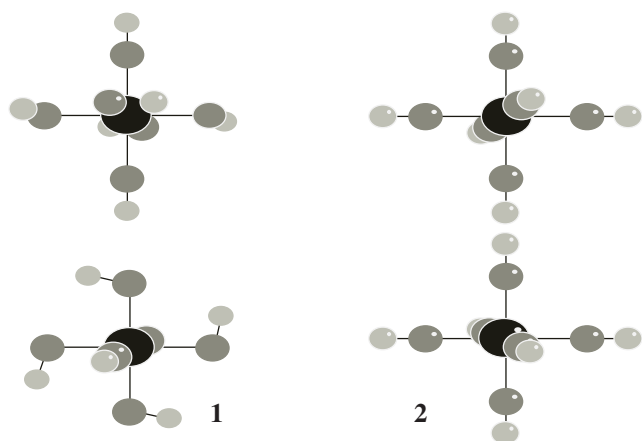


Fig. 1. Equilibrium structures of hexahydroxoplutonium clusters $\text{Pt}(\text{OH})_6^n$ with symmetry C_{4h} .

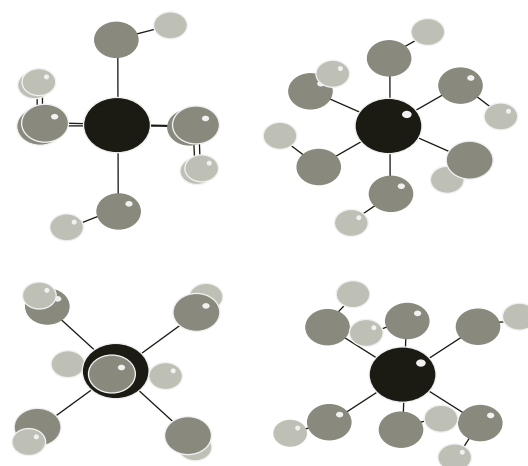


Fig. 2. Equilibrium structure of the hexahydroxoplutonium cluster $\text{Pt}(\text{OH})_6^n$ with symmetry C_i .

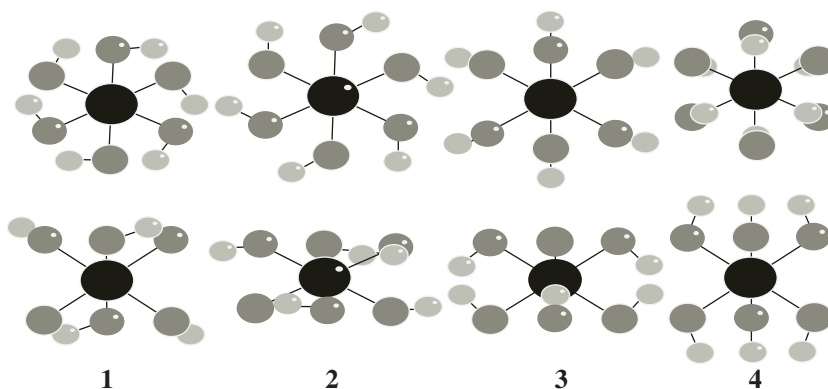


Fig. 3. Equilibrium structures of hexahydroxoplutonium clusters $\text{Pt}(\text{OH})_6^n$ with symmetry C_{3i} .

within the limits of PES minima, the clusters with octahedral symmetry have, as a rule, maximal energies. The energies at the points of PES minima for the other symmetries of different clusters (including those discarded from consideration) fall within this range and are strongly shifted to minimal energies.

The results of the $\text{Pt}(\text{OH})_6^{n-}$ geometry optimization for platinum in different oxidation states show that the clusters with a geometry other than octahedral have minimal energies (Table 1). Moreover, the clusters with the octahedral symmetry have the highest energy and anomalously short Pt–O distances. The PtOH angles for low-symmetry clusters are close to tetrahedral ones (Table 1), which points to the covalent nature of the platinum–oxygen bond. The low energy of the low-symmetry clusters confirms a high degree of covalence of the Pt–O bond, which is actually observed in synthesized complexes. The properties of $\text{Pt}(\text{OH})_6^{2-}$ and its derivatives are best described by symmetry C_{3i} .

The fact that the lowest energy configurations of the $\text{Pt}(\text{OH})_6^{n-}$ complexes at $n = -1$ and 0 have symmetry C_i is evidence that the system tends to reduce the cluster symmetry as the electron density at the complex-forming atom decreases. This can be caused by an increase in the degree of covalence of the platinum–ligand bond, leading to a decrease in the corresponding internuclear distance and, thus, the enhancement of the ligand–ligand interaction, as well as by the manifestation of the Jahn–Teller effect. However, the geometry optimization is performed for isolated clusters, whereas, in real systems, complexes experience the action of the environment (solvent, crystal field induced by counterions and other complexes), which changes the values of PES minima. It is evident that the system energy increases for low symmetries and decreases for some high symmetries determined by the environment. In particular, for hexagonal crystals, symmetry C_{3i} is expected to be the most favorable.

The equilibrium O–H distances obtained for virtually all hexahydroxoplatinum clusters vary within 0.98–0.99 Å, which corresponds to the distance in available hydroxo compounds. The Pt–O distances calculated for $\text{Pt}(\text{OH})_6^{2-}$ (1.954–1.961 Å) are consistent with known data [5, 10] for hexahydroxoplatinates (1.95 Å). This confirms once more the adequacy of the computational method used in this work and the soundness of the choice of quasirelativistic pseudopotentials for such objects.

The force constants and normal mode frequencies were calculated for the $\text{Pt}(\text{OH})_6^{2-}$ cluster with symmetry C_{3i} , which has the lowest energy for this symmetry group (Fig. 3, 1). The calculation of force constants for the 13-atom cluster gave 33 frequencies corresponding to 22 normal modes ($\Gamma = 5A_g + 5E_{2g} + 6B_u + 6E_{1u}$). Their assignment is presented in Table 2.

The Hartree–Fock force fields and frequencies of clusters are generally somewhat overestimated as compared to the experimental values due to the use of the harmonic approximation. Such a situation is observed for the calculated and experimental frequencies of $\text{Pt}(\text{OH})_6^{2-}$ (Table 2). In the high-frequency region, the difference is as large as 15–20%; however, it virtually vanishes as the frequency decreases.

To describe the electronic structure of compounds with heavy $5d$ atoms like platinum, the use of relativistic quantum mechanics is advisable. On the other hand, relativistic corrections should not play a decisive role in consideration of outer $5d6s$ electrons, which is supported by known calculations of atoms in heavy-metal compounds [12, 13]. Therefore, the choice of quasirelativistic pseudopotentials of Pt [9] for describing the clusters under consideration is justified.

The use of the Hartree–Fock method is limited for clusters with a considerable negative charge. Therefore, the above computation results can be considered only as an acceptable approximation. It is worth noting that the relation between the magnitudes of the energies of like clusters has a clear physical meaning. This is confirmed, in particular, by the monotonic decrease in the calculated energy of the $\text{Pt}(\text{OH})_6^{n-}$ clusters as a function of their symmetry, independent of their charge (Fig. 4).

Thus, using hexahydroxo complexes of platinum in different oxidation states as an example, we showed that the suggested computational method is valid for description of platinum-containing clusters and affords data consistent with the experimental data for known compounds.

Table 2. Normal mode frequencies for hexahydroxoplatinate $\text{Pt}(\text{OH})_6^{2-}$ (C_{3i} , $\Gamma = 5A_g + 5E_{2g} + 6B_u + 6E_{1u}$)

| ν , cm^{-1} | Symmetry of vibration | Type of vibration | ν , cm^{-1} | | |
|--------------------------|-----------------------|-----------------------|--------------------------|------|------------------------------------|
| | | | [3] | [11] | [14] (for PtF_6^{2-}) |
| 125.32 | E_{1u} | $\tau(\text{PtOH})$ | | | |
| 214.57 | A_g | $\delta(\text{OPtO})$ | | | 143 |
| 215.41 | E_{2g} | $\tau(\text{PtOH})$ | | | |
| 246.57 | B_u | $\tau(\text{PtOH})$ | | | |
| 278.53 | E_{1u} | $\delta(\text{OPtO})$ | | | 210 |
| 285.08 | B_u | $\delta(\text{OPtO})$ | | | |
| 288.35 | E_{2g} | $\delta(\text{OPtO})$ | 290 | | |
| 323.81 | E_{1u} | $\delta(\text{OPtO})$ | 328 | 301 | 281 |
| 408.5 | B_u | $\tau(\text{PtOH})$ | 350 | | |
| 411.8 | A_g | $\tau(\text{PtOH})$ | 470 | | |
| 611.24 | E_{1u} | $\nu(\text{PtO})$ | | 515 | |
| 620.72 | B_u | $\nu(\text{PtO})$ | 532 | 538 | 571 |
| 635.66 | E_{2g} | $\nu(\text{PtO})$ | 570 | | 576 |
| 652.51 | A_g | $\nu(\text{PtO})$ | 600 | | 611 |
| 1148.79 | A_g | $\delta(\text{PtOH})$ | 820 | | |
| 1153.97 | E_{2g} | $\delta(\text{PtOH})$ | | | |
| 1180.41 | B_u | $\delta(\text{PtOH})$ | | 1058 | |
| 1184.07 | E_{1u} | $\delta(\text{PtOH})$ | 1070 | 1076 | |
| 4060.42 | A_g | $\nu(\text{OH})$ | | | |
| 4062.52 | E_{2g} | $\nu(\text{OH})$ | | | |
| 4063.94 | B_u | $\nu(\text{OH})$ | | 3376 | |
| 4064.30 | E_{1u} | $\nu(\text{OH})$ | | | |

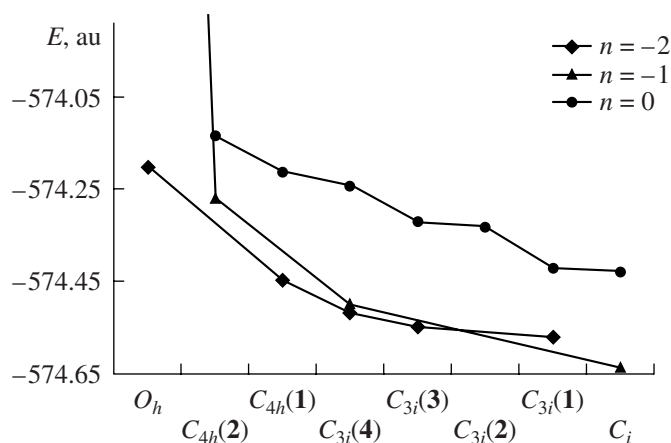


Fig. 4. Energy of the $\text{Pt}(\text{OH})_6^n$ clusters as a function of n and symmetry group.

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