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## Ab Initio Calculations of Hydroxoplatinum Compounds: II. Binuclear Platinum(IV) Superoxo Complexes

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**Abstract**—The structural and spectral data have been obtained by ab initio methods for the  $[(\text{OH})_4\text{Pt}(\mu\text{-O}_2)(\mu\text{-OH})\text{Pt}(\text{OH})_4]^{2-}$ ,  $[(\text{OH})_4\text{Pt}(\mu\text{-O}_2)(\mu\text{-OH})\text{Pt}(\text{OH})_4(\text{OH})]^{3-}$ ,  $[(\text{OH})_5\text{Pt}(\mu\text{-O}_2)\text{Pt}(\text{OH})_5]^{3-}$ , and  $[(\text{H}_2\text{O})(\text{OH})_4\text{Pt}(\mu\text{-O}_2)\text{Pt}(\text{OH})_4(\text{H}_2\text{O})]^-$  clusters, corresponding to binuclear platinum(IV) superoxo complexes with one and two bridges. The data obtained are in good agreement with experimental data and make it possible to judge the structure of available complexes.

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Previously [1, 2], it was shown that oxidative synthesis in alkaline solutions of Pt(IV) leads to different superoxoplatinum(IV) complexes. These compounds mainly exist in solution (only one compound was synthesized in the solid state [3]), and their structures were judged using the data of different physicochemical methods [4, 5].

This work deals with theoretical consideration of the possibility of the existence of similar platinum(IV) superoxo complexes and with the determination of their structural and spectral features. The applicability of this approach was shown in our previous work on clusters corresponding to the hexahydroxoplatinate(IV) ion [6].

A solution to the geometry optimization problem for the clusters corresponding to superoxo platinum derivatives should answer a number of questions, including (1) whether the formation of similar binuclear mono- and dibridged superoxo complexes is theoretically possible, (2) whether conformational isomerism is possible for these complexes, (3) how close the resulting geometric parameters are to the parameters for other known superoxo complexes, (4) how stable mono- or dibridged complexes are, and (5) what effect the superoxo group will have in vibrational spectra.

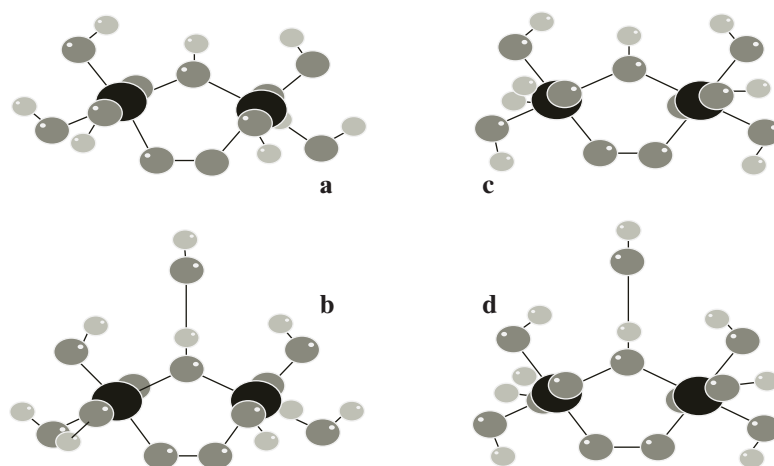
### COMPUTATIONAL DETAILS

The procedures and results described in [6] were used in calculations. The minima of the potential energy surfaces (PES) of the clusters corresponding to binuclear superoxohydroxoplatinum complexes with one and two bridges and their equilibrium geometric parameters were determined at the Hartree–Fock level of theory with the GAMESS [7] and PC GAMESS [8]

programs by the quasi-Newton–Raphson gradient method. Quasirelativistic [9, 10] 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 oxygen atoms, the quasirelativistic pseudopotential of the 1s inner shell with the  $(4s5p)/[2s3p]$  basis set was used [9]. 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 geometry 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.

For the determination of 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.



**Fig. 1.** Equilibrium structures of the binuclear dibridged platinum superoxo complexes  $[(\text{OH})_4\text{Pt}(\mu\text{-O}_2)(\mu\text{-OH})\text{Pt}(\text{OH})_4]^{2-}$  (**1**) and  $[(\text{OH})_4\text{Pt}(\mu\text{-O}_2)(\mu\text{-OH})\text{Pt}(\text{OH})_4 \cdot (\text{OH})]^{3-}$  (**2**).

In the determination of the geometric parameters of clusters, the platinum–oxygen distance was taken to be 1.95 Å [11, 12], and the oxygen–hydrogen distance was assumed to be 1 Å. The HOPl angle was varied from 180° to 90°. The initial oxygen–oxygen distance was taken to be 1.34 Å, which corresponded to the internuclear distance in bridging superoxo ligands in complexes [13, 14].

Calculations were performed for the binuclear superoxoplatinum complexes



with geometry optimization under the assumption of symmetry  $C_{2v}$  and  $C_{2h}$ , respectively, for each pair of complexes.

In the case of complex **2**, the equilibrium geometry was first found for cluster **1**, and then an  $\text{OH}^-$  group was added to the optimized cluster along the  $C_2$  axis at a distance of  $\sim 2.5$  Å corresponding to the hydrogen bond. This allowed us to compare the energies of clusters **2** and **3**, since they have the same number of atoms and electrons.

The starting geometry of complex **4** was based on the optimized structure of cluster **3**, with the difference that  $\text{H}_2\text{O}$  molecules were substituted for the OH groups in the axial positions to the superoxo oxygen, which led to a decrease in the total charge of the system to  $-1$  without considerable change in the state of platinum and superoxo oxygen.

During geometry optimization, different mutual arrangements of  $\text{OH}^-$  groups with respect to each other and to the superoxo group ( $\text{O}_2^-$ ) were considered by gradually changing the OPtOH torsion angles. In addition, for the monobridged complex, the hydroxide groups were placed both in the Pt–O–Pt plane and out of this plane (at an angle of  $\approx 45^\circ$  to this plane). For the dibridged complex, the additional (“excessive”)  $\text{OH}^-$  group was placed both in the region of the hydroxo bridge and in the region of the superoxo bridge. Notwithstanding a large number of variants considered for the structure of platinum superoxo complexes, the number of structures corresponding to PES minima turned out to be limited (Figs. 1–3, Tables 1–3).

## RESULTS AND DISCUSSION

The geometry optimization results confirmed that the PES of binuclear superoxo complexes of each type has several local minima close in energy, which correspond to different conformations of the clusters (Tables 1–3). All stable conformations (Figs. 1–3) can be derived from each other by gradually rotating the hydroxo groups with respect to the Pt–OH bonds. As in the case of the hexahydroxo complexes [6], the PtOH angles are close to tetrahedral, which points to the covalent character of the Pt–OH bonds. The HOH angle of the aqua ligand in virtually all clusters of type **4** is  $109^\circ$ . The O–H bond lengths in all clusters are the same as expected for the  $\text{OH}^-$  ion. The distances between the platinum atom and the hydroxide oxygen atom are in the range 1.9–2.1 Å (Tables 1–3) and depend on the bond position with respect to the superoxo group and on the type of cluster (in particular, on the presence of aqua ligands). The shortest bond length is observed for

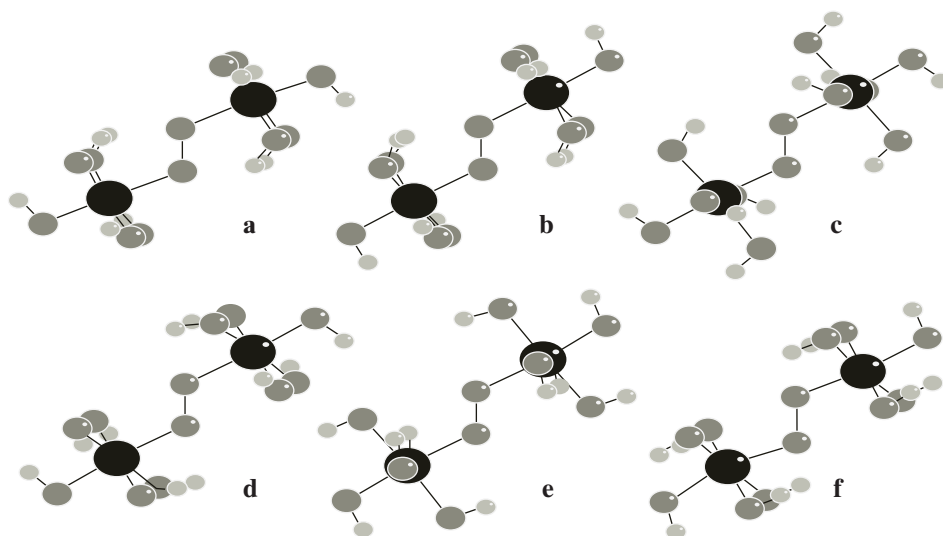


Fig. 2. Equilibrium structure of the binuclear monobridged platinum superoxo complexes  $[(\text{OH})_5\text{Pt}(\mu\text{-O}_2)\text{Pt}(\text{OH})_5]^{3-}$  (**3**).

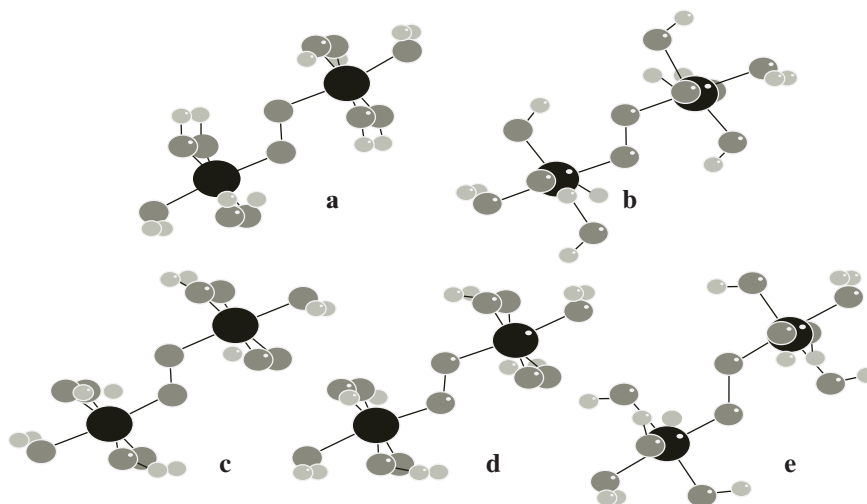


Fig. 3. Equilibrium structures of the binuclear monobridged platinum superoxo complexes  $[(\text{H}_2\text{O})(\text{OH})_4\text{Pt}(\mu\text{-O}_2)\text{Pt}(\text{OH})_4(\text{H}_2\text{O})]^-$  (**4**).

the  $\text{OH}^-$  group in the axial position to the  $\text{O}_2^-$  group (in the most stable conformations of cluster **3**, Table 2). On the other hand, in all complexes in the most stable conformations, the longest Pt–O bond (about 2.04 Å) involves the superoxo group (about 1.93 Å in type **4** clusters). The other Pt–OH bond lengths fall within this range and are close to the bond lengths in hexahydroxoplatinate(IV). These bond lengths indicate that the Pt– $\text{O}_2^-$  bond is rather spatially extended and that the electron density is considerably shifted from the platinum atom to this bond.

The O–O distance in the superoxo group virtually in all complexes (**2** and **3**) differs slightly from the value expected from the literature data (1.34 Å) and equals

~1.37 Å (1.36 Å for **4**). It should be noted that, in addition to the error of calculation, this distance is very sensitive to a change in the population of the antibonding orbitals of the  $\text{O}_2^-$  group [15] and should increase as the electron density is shifted from the platinum atom.

The same is true for the ligand environment of the central atom. In particular, the substitution of aqua groups for two hydroxyl groups in cluster **3** (resulting in cluster **4**) leads to a change in geometric parameters (in particular, in Pt–O bond lengths).

Variation in the energy of clusters **3** and **4** as a function of their geometry shows that intramolecular hydrogen bonds between the atoms of the  $\text{OH}^-$  group and the

**Table 1.** Results of quantum-chemical calculations of the binuclear dibridged platinum superoxo complexes  $[(\text{OH})_4\text{Pt}(\mu\text{-O}_2)(\mu\text{-OH})\text{Pt}(\text{OH})_4]^{2-}$  (**1**) and  $[(\text{OH})_4\text{Pt}(\mu\text{-O}_2)(\mu\text{-OH})\text{Pt}(\text{OH})_4(\text{OH})]^{3-}$  (**2**)

Cluster conformation*	$R(\text{Pt}-\mu\text{-O}_2^-)$ , Å	$R(\text{Pt}-\mu\text{-OH}^-)$ , Å	$R(\text{Pt}-\text{OH}^-)$ , Å	$R(\text{O}-\text{O})$ , Å	$R(\mu\text{-OH}^--\text{OH}^-)$ , Å	Cluster energy, au
<b>a</b>	2.026	1.993	1.907	1.367		-1073.151
			1.911			
			1.940			
			1.940			
<b>b</b>	2.025	1.979	1.908	1.367	2.079	-1147.855
			1.916			
			1.941			
			1.941			
<b>c</b>	2.026	1.987	1.910	1.364		-1073.148
			1.917			
			1.937			
			1.937			
<b>d</b>	1.941	1.971	1.984	1.493	2.114	-1147.827
			1.935			
			1.955			
			1.955			

\* Corresponds to the number of the conformation in Fig. 1.

$\text{O}_2^-$  group should contribute considerably to cluster stabilization. In particular, the lowest-lying conformations have five-membered rings (Fig. 2, structures a–c; Fig. 3, structures a and b) formed by two oxygen atoms of the superoxo group, the platinum atom, the oxygen atom of the equatorial hydroxo group, and its hydrogen atom, which closes the ring through the hydrogen bond involving the first oxygen atom ( $R(\text{H}\cdots\text{O}) \approx 2.2\text{--}2.4$  Å).

Comparison of the geometric parameters of clusters **2** and **3** shows that the introduction of a hydroxide ion as an additional dipole into the system can lead to a change in the geometric parameters of the initial complex (compare, for example,  $R(\text{O}-\text{O})$ , Table 1). This observation, as well as the above fact that hydrogen bonding is responsible for stabilization, should point to the considerable sensitivity of similar complexes (their geometry and stability) to the properties of the surrounding medium. Hence, the solvent is precisely what should determine the possibility of formation of a definite type of complex with a definite conformation and its geometric parameters, which agrees with what is actually observed [1, 2].

Comparison of clusters **2** and **3** shows that a monobridged superoxo complex should be more stable than a dibridged complex since the latter with a rigid five-membered ring is obviously a stressed structure.

For lowest-lying clusters (**1a** in Fig. 1a and **3a** in Fig. 2a), the force constants and normal mode frequencies were calculated. For each cluster, 60 and 66 normal mode frequencies were obtained, and their assignment is presented in Tables 4<sup>1</sup> and 5<sup>2</sup>, respectively.

Analysis of the calculated normal modes for platinum superoxo complexes shows that virtually all of them are due to interactions of  $\text{OH}^-$  ligands with platinum. The only characteristic vibration due to the  $\text{O}_2^-$  group can be the stretching vibration  $\nu(\text{O}-\text{O})$  (1463 and 1437  $\text{cm}^{-1}$  for each cluster, respectively). This vibration is alone in a relatively isolated spectral region (the nearest vibration is lower in frequency by about 200  $\text{cm}^{-1}$ ) and cannot be erroneously interpreted.

The ab initio force fields and frequencies for the clusters under consideration obtained in the harmonic approximation at the Hartree–Fock level should be overestimated as compared to the experimental data. Such a situation is observed for the calculated and experimental frequencies of  $\text{Pt}(\text{OH})_6^{2-}$  [6]. Applying

<sup>1</sup> For symmetry  $C_{2v}$ , the representation character is  $\Gamma = 19A_1 + 11A_2 + 18B_1 + 12B_2$ .

<sup>2</sup> For symmetry  $C_{2h}$ , the representation character is  $\Gamma = 19A_g + 15A_u + 14B_g + 18B_u$ .

**Table 2.** Results of quantum-chemical calculations of the binuclear monobridged platinum superoxo complexes  $[(\text{OH})_5\text{Pt}(\mu\text{-O}_2)\text{Pt}(\text{OH})_5]^{3-}$  (**3**)

Cluster conformation*	$R(\text{Pt}-\mu\text{-O}_2^-)$ , Å	$R(\text{Pt}-\text{axial OH}^-)$ , Å	$R(\text{Pt}-\text{OH}^-)$ , Å	$R(\text{O}-\text{O})$ , Å	Cluster energy, au
<b>a</b>	2.045	1.906	1.940 1.940 1.960 1.960	1.370	-1147.922
<b>b</b>	2.048	1.906	1.946 1.946 1.955 1.955	1.369	-1147.920
<b>c</b>	2.044	1.906	1.957 1.942 1.951 1.951	1.365	-1147.915
<b>d</b>	2.045	1.906	1.960 1.960 1.944 1.944	1.357	-1147.910
<b>d</b>	2.041	1.909	1.953 1.947 1.951 1.951	1.362	-1147.907
<b>f</b>	1.931	1.973	1.927 1.927 1.915 1.915	1.468	-1147.756

\* Corresponds to the index of the conformation in Fig. 2.

**Table 3.** Results of quantum-chemical calculations of the binuclear monobridged platinum superoxo complexes  $[(\text{H}_2\text{O})(\text{OH})_4\text{Pt}(\mu\text{-O}_2)\text{Pt}(\text{OH})_4(\text{H}_2\text{O})]^-$  (**4**)

Cluster conformation*	$R(\text{Pt}-\mu\text{-O}_2^-)$ , Å	$R(\text{Pt}-\text{OH}_2)$ , Å	$R(\text{Pt}-\text{OH}^-)$ , Å	$R(\text{O}-\text{O})$ , Å	Cluster energy, au
<b>a</b>	1.934	1.983	1.929 1.929 1.936 1.936	1.362	-1149.301
<b>b</b>	1.935	1.981	1.938 1.929 1.931 1.931	1.360	-1149.297
<b>c</b>	1.934	1.984	1.938 1.938 1.929 1.929	1.358	-1149.296
<b>d</b>	1.932	1.983	1.949 1.949 1.919 1.919	1.354	-1149.290
<b>f</b>	1.873	2.010	1.939 1.929 1.932 1.932	1.652	-1149.095

\* Corresponds to the index of the conformation in Fig. 3.

**Table 4.** Normal mode frequencies of the binuclear dibridged platinum superoxo complex  $[(\text{OH})_4\text{Pt}(\mu\text{-O}_2)(\mu\text{-OH})\text{Pt}(\text{OH})_4]^{2-}$  (**1a**) ( $C_{2v}$ ,  $\Gamma = 19A_1 + 11A_2 + 18B_1 + 12B_2$ )

$\nu$ , $\text{cm}^{-1}$	Symmetry	Type	$\nu$ , $\text{cm}^{-1}$	Symmetry	Type	$\nu$ , $\text{cm}^{-1}$	Symmetry	Type
613.08	$B_1$	$\tau(\text{PtOH})$	287.29	$B_1$	$\delta(\text{OPtO})$	712.94	$B_1$	$\nu(\text{PtO})$
451.88	$A_2$	$\tau(\text{PtOH})$	303.74	$B_2$	$\delta(\text{OPtO})$	1127.85	$A_2$	$\delta(\text{PtOH})$
409.71	$B_1$	$\tau(\text{PtOH})$	315.49	$B_1$	$\tau(\text{PtOH})$	1131.66	$B_1$	$\delta(\text{PtOH})$
261.18	$A_2$	$\tau(\text{PtOH})$	320.32	$A_2$	$\tau(\text{PtOH})$	1131.74	$B_1$	$\delta(\text{PtOH})$
205.36	$B_1$	$\tau(\text{PtOH})$	338.59	$A_1$	$\delta(\text{PtOH})$	1177.06	$A_1$	$\delta(\text{PtOH})$
137.8	$B_2$	$\tau(\text{PtOH})$	343.61	$B_1$	$\text{tr}(\mu\text{-OH})$	1182.84	$B_1$	$\delta(\text{PtOH})$
43.95	$A_2$	rot	374.91	$B_2$	$\text{tr}(\text{OO})$	1185.82	$A_1$	$\delta(\text{PtOH})$
80.49	$B_1$		401.94	$A_2$	$\tau(\text{PtOH})$	1214.87	$B_1$	$\delta(\text{PtOH})$
126.35	$A_1$	$\tau(\text{PtOH})$	411.21	$B_1$	$\tau(\text{PtOH})$	1230.01	$A_1$	$\delta(\text{PtOH})$
138.57	$A_1$	$\tau(\text{PtOH})$	444.04	$A_1$	$\text{tr}(\text{OO})$	1263.88	$B_1$	$\delta(\text{PtOH})$
139.29	$A_2$		539.87	$A_1$	$\text{tr}(\mu\text{-OH})$	1462.88	$A_1$	$\nu(\text{OO})$
173.49	$A_1$	$\tau(\text{PtOH})$	625.38	$B_2$	$\text{rot}(\text{OO})$	4026.73	$B_1$	$\nu(\text{OH})$
190.56	$B_1$	rot	638.40	$A_2$	$\nu(\text{PtO})$	4027.03	$A_1$	$\nu(\text{OH})$
238.77	$B_2$	$\text{tr}(\text{OO})$	639.68	$B_1$	$\text{rot}(\text{OO})$	4027.94	$A_1$	$\nu(\text{OH})$
270.55	$A_2$	$\text{rot}(\text{OO})$	656.78	$B_2$	$\nu(\text{PtO})$	4028.94	$B_2$	$\nu(\text{OH})$
275.12	$B_1$	$\tau(\text{PtOH})$	664.96	$B_1$	$\nu(\text{PtO})$	4029.89	$B_1$	$\nu(\text{OH})$
278.43	$A_2$	$\tau(\text{PtOH})$	665.89	$A_1$	$\nu(\text{PtO})$	4030.57	$A_1$	$\nu(\text{OH})$
280.01	$B_1$	$\tau(\text{PtOH})$	697.11	$B_1$	$\nu(\text{PtO})$	4045.07	$B_1$	$\nu(\text{OH})$
281.27	$A_1$	$\delta(\text{OPtO})$	698.48	$A_1$	$\nu(\text{PtO})$	4045.54	$A_1$	$\nu(\text{OH})$
286.65	$A_1$	$\delta(\text{OPtO})$	707.21	$A_1$	$\nu(\text{PtO})$	4141.73	$A_1$	$\nu(\text{OH})$

**Table 5.** Normal mode frequencies of the binuclear monobridged platinum superoxo complex  $[(\text{OH})_5\text{Pt}(\mu\text{-O}_2)\text{Pt}(\text{OH})_5]^{3-}$  (**3a**) ( $C_{2h}$ ,  $\Gamma = 19A_g + 15A_u + 14B_g + 18B_u$ )

$\nu$ , $\text{cm}^{-1}$	Symmetry	Type	$\nu$ , $\text{cm}^{-1}$	Symmetry	Type	$\nu$ , $\text{cm}^{-1}$	Symmetry	Type
24.52	$A_u$		295.62	$A_u$	$\tau(\text{PtOH})$	701.76	$A_g$	$\nu(\text{PtO})$
23.73	$B_g$		305.53	$A_g$	$\tau(\text{PtOH})$	1137.72	$B_g$	$\delta(\text{PtOH})$
22.16	$A_u$		318.19	$B_g$	$\tau(\text{PtOH})$	1140.07	$A_u$	$\delta(\text{PtOH})$
70.74	$B_u$		328.99	$B_u$	$\delta(\text{OPtO})$	1175.19	$B_u$	$\delta(\text{PtOH})$
89.96	$A_g$		336.40	$A_u$	$\tau(\text{PtOH})$	1183.60	$A_g$	$\delta(\text{PtOH})$
94.56	$B_g$	$\delta(\text{PtOH})$	345.56	$B_u$	$\tau(\text{PtOH})$	1198.49	$B_u$	$\delta(\text{PtOH})$
102.30	$A_u$	$\delta(\text{PtOH})$	345.69	$A_g$	$\tau(\text{PtOH})$	1200.56	$A_u$	$\delta(\text{PtOH})$
149.85	$A_g$		364.77	$B_u$	$\tau(\text{PtOH})$	1201.07	$B_g$	$\delta(\text{PtOH})$
157.43	$A_u$	$\delta(\text{PtOH})$	393.70	$A_u$	$\nu(\text{PtOH})$	1203.92	$A_g$	$\delta(\text{PtOH})$
159.77	$B_g$	$\delta(\text{PtOH})$	416.12	$B_u$	$\tau(\text{PtOH})$	1265.91	$A_g$	$\delta(\text{PtOH})$
220.64	$B_g$	$\tau(\text{PtOH})$	464.36	$B_u$	$\nu(\text{PtOO})$	1266.65	$B_g$	$\delta(\text{PtOH})$
254.51	$A_g$	$\tau(\text{PtOH})$	467.27	$A_g$	$\tau(\text{PtOH})$	1436.85	$A_g$	$\nu(\text{OO})$
256.43	$B_u$	$\tau(\text{PtOH})$	613.38	$A_g$	$\nu(\text{PtOO})$	4046.64	$B_g$	$\nu(\text{OH})$
257.81	$B_g$	$\tau(\text{PtOH})$	616.72	$B_g$	$\nu(\text{PtO})$	4047.00	$A_u$	$\nu(\text{OH})$
260.53	$A_u$	$\delta(\text{OPtO})$	623.47	$B_u$	$\nu(\text{PtO})$	4047.77	$B_u$	$\nu(\text{OH})$
272.14	$B_u$	$\delta(\text{OPtO})$	626.40	$A_u$	$\nu(\text{PtO})$	4048.36	$A_g$	$\nu(\text{OH})$
276.37	$B_u$	$\text{tr}(\text{OO})$	630.64	$A_g$	$\nu(\text{PtO})$	4050.43	$A_g$	$\nu(\text{OH})$
281.11	$B_u$	$\delta(\text{OPtO})$	649.21	$B_g$	$\nu(\text{PtO})$	4050.67	$B_u$	$\nu(\text{OH})$
281.16	$A_u$	$\delta(\text{OPtO})$	651.80	$A_u$	$\nu(\text{PtO})$	4053.99	$B_g$	$\nu(\text{OH})$
290.39	$B_g$		660.10	$B_u$	$\nu(\text{PtO})$	4054.00	$A_u$	$\nu(\text{OH})$
293.29	$A_g$	$\delta(\text{OPtO})$	660.62	$A_g$	$\nu(\text{PtO})$	4056.92	$A_g$	$\nu(\text{OH})$
294.02	$B_u$	$\delta(\text{OPtO})$	699.93	$B_u$	$\nu(\text{PtO})$	4057.12	$B_u$	$\nu(\text{OH})$



the correction 15–20% used in [6] to the superoxo complexes, we obtain **1a**  $\nu(\text{O-O}) \approx 1240\text{--}1170\text{ cm}^{-1}$  for cluster **1a** and **3a**  $\nu(\text{O-O}) \approx 1220\text{--}1150\text{ cm}^{-1}$  for cluster **3a**. Taking into account the approximate calculation and the effect of the solvent and ligands, these values are consistent with the experimental data (1060 and  $1020\text{ cm}^{-1}$ , respectively) obtained for solutions of platinum superoxo complexes [4].

Thus, our quantum-chemical calculations confirm the possibility of formation and stability of binuclear platinum(IV) superoxo complexes of different types and conformations, are in agreement with the known experimental data, and predict the high sensitivity of such complexes to external conditions.

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