

Theoretical Study of Far-Infrared Spectra of Some Palladium and Platinum Halide Complexes

Lin Zhang, Hua Wei, Yu Zhang, Zijian Guo, and Longgen Zhu*

State Key Laboratory of Coordination Chemistry, Coordination Chemistry Institute, Nanjing University, Nanjing, 210093, China

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The far-infrared spectra of palladium and platinum halide complexes, MX_4^{2-} and $\text{M}_2\text{X}_6^{2-}$, have been studied for the first time using ab initio restricted Hartree–Fock method with the LANL2DZ basis set. The calculated vibrational frequencies, scaled with a uniform factor of 1.12, are in good agreement with the measured values. Moreover, some vibrational frequencies are predicted for palladium and platinum complexes that are difficult to measure.

Introduction

In the past decade, the development of ab initio methods has led to its application to chemically interesting problems including metal complexes. The quantum chemical methods are able to predict electronic structures,^{1–2} bonding characteristics,^{3–5} interaction mechanisms,^{6–8} optical^{9–10} and magnetic¹¹ properties, etc. The ab initio calculations of vibrational spectra, which has been primarily restricted to organic compounds and small polyatomic systems,^{12–16} were recently developed for transition metal complexes.¹⁷ Most of the computations were performed by the HF, MP2, BP86, and BLYP methods.^{18–26} We report here the far-infrared spectra of some planar palladium and platinum complexes, using the ab initio restricted Hartree–Fock (RHF) method.

Our interest on Pd and Pt complexes is motivated by their antitumor activities²⁷ and ability to hydrolyze peptides and proteins.^{28–29} Most of the Pd and Pt complexes synthesized as antitumor drugs and cleavage agents are square planar complexes, like the MX_4^{2-} and $\text{M}_2\text{X}_6^{2-}$ ($\text{M} = \text{Pd}, \text{Pt}$; $\text{X} = \text{Cl}$) compounds. Therefore, a theoretical study of their skeletal vibrations is of interest and the far-infrared spectra calculated are compared with the literature data.

Calculation

Geometry optimization is one of the most important steps in the theoretical calculation of vibrational spectra. The critical problem for metal complexes, of the second- and third-row transition metals, is the relativistic effect that must be properly dealt with in the computation. As this study involves Pd and Pt, we employed an effective core potential. In the present work, the geometry optimizations of MX_4^{2-} and $\text{M}_2\text{X}_6^{2-}$ ($\text{M} = \text{Pd}, \text{Pt}$; $\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{and I}$) were performed using the Gaussian 94 program³⁰ generated by Cerius2, with RHF/LANL2DZ (Los Alamos ECP plus DZ) basis set. The theoretical results were scaled with a uniform factor of $\nu^{\text{ex}}/\nu^{\text{calcd}}$ from a comparison with experimental data determined in solution.

Results and Discussion

Geometries. The fully optimized geometries of MX_4^{2-} and $\text{M}_2\text{X}_6^{2-}$, shown in Figure 1, have square planar configurations

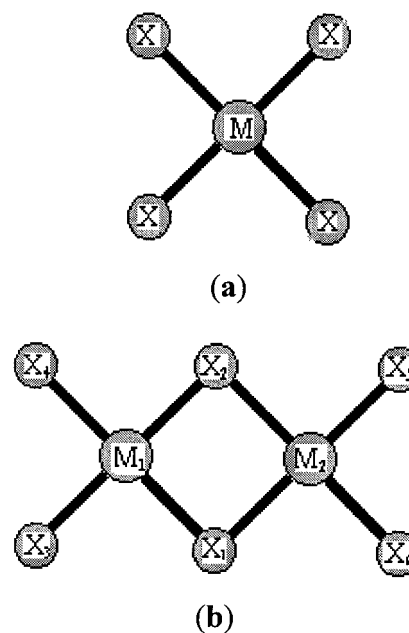


Figure 1. (a) Optimized geometry of MX_4^{2-} . (b) Optimized geometry of $\text{M}_2\text{X}_6^{2-}$.

while the $\text{M}_2\text{X}_6^{2-}$ complexes are halide bridged planar molecules. The bond lengths and angles calculated are presented in Tables 1 and 2, along with available experimental data. The optimized bond length of Pt–Cl in PtCl_4^{2-} is 2.48 Å, and is about 0.15 and 0.22 Å longer when compared to the observed values in K_2PtCl_4 and in $(\text{NH}_4)_2\text{PtCl}_4$, respectively, where different cations make the Pt–Cl bond lengths different in some extent. The calculated Pd–Cl bond length is 2.47 Å, which is 0.16 Å longer than the observed value in K_2PdCl_4 .

A similar tendency is also found in $\text{M}_2\text{X}_6^{2-}$. Here the calculated bond lengths are 0.12–0.22 Å longer than those that have been measured. The trend is more evident for bond lengths formed by bridging halide and metal atoms. These differences between the calculated and measured bond lengths are quite substantial, considering that optimized geometries are anionic compounds without counterions, and that electron correlation deficiencies are involved. In $\text{M}_2\text{X}_6^{2-}$ complexes, the maximum deviation between the calculated and experimental bond angles is $\pm 3^\circ$. The optimized bond angles ($\text{M}_1\text{X}_1\text{M}_2$), ($\text{M}_1\text{X}_2\text{M}_2$),

* To whom correspondence should be addressed.

TABLE 1: Bond Lengths (Å) of MX₄²⁻ Complexes

| anion | PdF ₄ ²⁻ | PdCl ₄ ²⁻ | PdBr ₄ ²⁻ | PdI ₄ ²⁻ | PtF ₄ ²⁻ | PtCl ₄ ²⁻ | PtBr ₄ ²⁻ | PtI ₄ ²⁻ |
|---------------------|--------------------------------|---------------------------------|---------------------------------|--------------------------------|--------------------------------|---------------------------------|---------------------------------|--------------------------------|
| calcd | 2.03 | 2.47 | 2.63 | 2.81 | 2.04 | 2.48 | 2.63 | 2.80 |
| exptl ³¹ | | 2.31 | | | | 2.33 | | |

TABLE 2: Optimized Bond Lengths (Å) and Bond Angles (deg) of M₂X₆²⁻ Complexes

| | Pd ₂ F ₆ ²⁻ | Pd ₂ Cl ₆ ²⁻ | Pd ₂ Br ₆ ²⁻ | Pd ₂ I ₆ ²⁻ | Pt ₂ F ₆ ²⁻ | Pt ₂ Cl ₆ ²⁻ | Pt ₂ Br ₆ ²⁻ | Pt ₂ I ₆ ²⁻ |
|--|--|---|---|--|--|---|---|--|
| <i>r</i> (M ₁ -X ₁) | 2.10 | 2.52 | 2.65 2.45 ^a | 2.79 | 2.11 | 2.52 2.33 | 2.64 2.41 | 2.78 |
| <i>r</i> (M ₂ -X ₁) | 2.10 | 2.52 | 2.65 2.45 | 2.79 | 2.11 | 2.52 2.33 | 2.64 2.41 | 2.78 |
| <i>r</i> (M ₁ -X ₂) | 2.10 | 2.52 | 2.65 2.45 | 2.79 | 2.11 | 2.52 2.34 | 2.64 2.45 | 2.78 |
| <i>r</i> (M ₂ -X ₂) | 2.10 | 2.52 | 2.65 2.45 | 2.79 | 2.11 | 2.52 2.32 | 2.64 2.45 | 2.78 |
| <i>r</i> (M ₁ -X ₃) | 1.98 | 2.41 | 2.56 2.41 | 2.74 | 1.99 | 2.42 2.28 | 2.57 2.45 | 2.74 |
| <i>r</i> (M ₁ -X ₄) | 1.98 | 2.41 | 2.56 2.42 | 2.74 | 1.99 | 2.42 2.27 | 2.57 2.42 | 2.74 |
| <i>r</i> (M ₂ -X ₃) | 1.98 | 2.41 | 2.56 2.41 | 2.74 | 1.99 | 2.42 2.27 | 2.57 2.45 | 2.74 |
| <i>r</i> (M ₂ -X ₆) | 1.98 | 2.41 | 2.56 2.42 | 2.74 | 1.99 | 2.42 2.28 | 2.57 2.42 | 2.74 |
| <i>a</i> (M ₁ X ₁ M ₂) | 104 | 98 | 96 94 | 96 | 104 | 98 94 | 96 93 | 96 |
| <i>a</i> (M ₁ X ₂ M ₂) | 104 | 98 | 96 94 | 96 | 104 | 98 95 | 96 93 | 96 |
| <i>a</i> (X ₁ M ₁ X ₂) | 76 | 82 | 84 86 | 84 | 76 | 83 85 | 84 86 | 84 |
| <i>a</i> (X ₁ M ₂ X ₂) | 76 | 82 | 84 86 | 84 | 76 | 83 85 | 84 86 | 84 |
| <i>a</i> (X ₂ M ₂ X ₅) | 96 | 93 | 92 92 | 92 | 97 | 93 91 | 92 90 | 92 |
| <i>a</i> (X ₁ M ₂ X ₆) | 96 | 93 | 92 92 | 92 | 97 | 93 91 | 92 90 | 92 |
| <i>a</i> (X ₂ M ₁ X ₄) | 96 | 93 | 92 92 | 92 | 97 | 93 91 | 92 90 | 92 |
| <i>a</i> (X ₁ M ₁ X ₃) | 96 | 93 | 92 92 | 92 | 97 | 93 91 | 92 90 | 92 |
| <i>a</i> (X ₃ M ₁ X ₄) | 92 | 93 | 92 91 | 92 | 91 | 92 93 | 93 94 | 93 |
| <i>a</i> (X ₅ M ₂ X ₆) | 92 | 93 | 92 91 | 92 | 91 | 92 92 | 93 94 | 93 |

^a The values in italic are experimental data: Pd₂Br₆²⁻ from ref 32, Pt₂Cl₆²⁻ from ref 33, and Pt₂Br₆²⁻ from ref 34.

(X₂M₁X₄), (X₁M₁X₃), (X₂M₂X₅), and (X₁M₂X₆) are larger than the experimental values, while those of (X₁M₁X₂), (X₁M₂X₂), (X₃M₁X₄), and (X₅M₂X₆) are smaller.

Although all the calculated bond lengths are overestimated to some extent, the calculated vibrational frequencies are satisfactory and in good agreement with the solvent spectra.

Vibrational Frequencies. MX₄²⁻ The compounds have a square planar configuration and belong to the *D*_{4h} point group. Vibrational analysis for this point group indicates that MX₄²⁻ has seven fundamental modes of vibrations, with three of them IR active. Among the IR fundamentals, the two belonging to the E_u representation are an in-plane stretching ν₆, and an in-plane bending ν₇, while the third one, A_{2u}, is an out-of-plane mode ν₃.

For a comparison of the calculated vibrational frequencies with experimental frequencies, a uniform scale factor $\nu^{\text{ex}}/\nu^{\text{calcd}}$ was introduced.³⁵ As most calculations were performed at the ab initio SCF level, the calculated harmonic frequencies are usually higher than the observed values, and the scaling factor is smaller than 1.0. In our case, a scale factor of 1.12 was chosen for the complexes studied here. This difference is mainly due to the overestimation of the bond lengths by the RHF method. Overestimation by 0.1 to 0.3 Å produces lower vibrational frequencies and higher IR intensities. Similar phenomena are

found for the M₂X₆²⁻ species, shown in Tables 3 and 4. In addition, both electron correction effect and anharmonicity usually lead to lower fundamentals.

Table 3 shows the calculated, scaled and experimentally determined vibrational frequencies. As shown in the table, the scaled vibrational frequencies are consistent with those of R₂-MX₄ (R=Buⁿ₄N⁺) in solution where R₂MX₄ is present as the MX₄²⁻ anion. The maximum deviation is found to be ±12 cm⁻¹. As indicated in Table 3, the frequencies of solid K₂MX₄ are always higher than those of R₂MX₄ in solution, except for ν₃A_{2u} of PdCl₄²⁻. It is evident that the interaction between cation and anion in K₂MX₄ crystals affects the vibrational frequencies, and as a result the calculated vibrational frequencies are consistently lower than those of K₂MX₄ in the solid state with maximum deviation of -43 cm⁻¹.

It is worth mentioning that the vibrations of MX₄²⁻ compounds are sometimes assigned³⁷ on the assumption that the frequencies in far-infrared region follow the order ν₆E_u > ν₇E_u > ν₃A_{2u}. However, according to our calculations, this order is not always correct. It is satisfactory only for PdCl₄²⁻, PtCl₄²⁻ and PtBr₄²⁻; while for PdBr₄²⁻, PdI₄²⁻, and PtI₄²⁻, the order should be reassigned as ν₆E_u > ν₃A_{2u} > ν₇E_u.

M₂X₆²⁻ These complexes belong to *D*_{2h} point group. The B_{nu} (*n* = 1, 2, or 3) modes are IR active. B_{1g}ν₉ is an out-of-plane

TABLE 3: Vibrational Frequencies of MX_4^{2-} (Scaling Factor = 1.12)

| anion | calcd (IR int.) | scaled | a^{36} | b^{37-39} | assignment |
|----------------------|-----------------|--------|--------------------|-------------|-------------------------------------|
| PdF_4^{2-} | 470(200) | 526 | | | $\nu_6 E_u$ M-X stretching |
| | 234(10) | 262 | | | $\nu_7 E_u$ in-plane bending |
| | 224(68) | 251 | | | $\nu_3 A_{2u}$ out-of-plane bending |
| PdCl_4^{2-} | 292(123) | 327 | 321(10) | 336s | $\nu_6 E_u$ M-X stretching |
| | 145(0) | 162 | 161(sh) | 193m | $\nu_7 E_u$ in-plane bending |
| | 141(27) | 158 | 150(1) | | $\nu_3 A_{2u}$ out-of-plane bending |
| PdBr_4^{2-} | 217(72) | 243 | 243vs ^c | 260s | $\nu_6 E_u$ M-X stretching |
| | 93(2) | 104 | 104w ^c | 140sh | $\nu_7 E_u$ in-plane bending |
| | 110(8) | 123 | 114wm ^c | 130s | $\nu_3 A_{2u}$ out-of-plane bending |
| PdI_4^{2-} | 177(59) | 198 | | | $\nu_6 E_u$ M-X stretching |
| | 71(5) | 80 | | | $\nu_7 E_u$ in-plane bending |
| | 94(3) | 105 | | | $\nu_3 A_{2u}$ out-of-plane bending |
| PtF_4^{2-} | 468(199) | 524 | | | $\nu_6 E_u$ M-X stretching |
| | 230(12) | 258 | | | $\nu_7 E_u$ in-plane bending |
| | 212(40) | 237 | | | $\nu_3 A_{2u}$ out-of-plane bending |
| PtCl_4^{2-} | 277(107) | 310 | 313(10) | 321s | $\nu_6 E_u$ M-X stretching |
| | 143(2) | 160 | 165(0) | 191w | $\nu_7 E_u$ in-plane bending |
| | 126(20) | 141 | 147(1) | 168w | $\nu_3 A_{2u}$ out-of-plane bending |
| PtBr_4^{2-} | 192(58) | 215 | 227(10) | 232s | $\nu_6 E_u$ M-X stretching |
| | 94(0) | 106 | 112(sh) | 135m | $\nu_7 E_u$ in-plane bending |
| | 93(5) | 105 | 105(1) | 135m | $\nu_3 A_{2u}$ out-of-plane bending |
| PtI_4^{2-} | 153(46) | 171 | | 180 | $\nu_6 E_u$ M-X stretching |
| | 75(2) | 84 | | 127 | $\nu_7 E_u$ in-plane bending |
| | 79(2) | 88 | | 105 | $\nu_3 A_{2u}$ out-of-plane bending |

^a In $(\text{Bu}^n_4\text{N})_2\text{MX}_4$ solution. ^b In $K_2\text{MX}_4$ solid salts. ^c In $(\text{Bu}^n_4\text{N})_2\text{PdBr}_4$ mull.

MX_2 wag. Previously, the $B_{2u}\nu_{12}$ and $B_{3u}\nu_{16}$ modes were assigned to the terminal stretches, and the $B_{2u}\nu_{13}$ and $B_{3u}\nu_{17}$ to bridging stretches. In fact, there is no reliable way to distinguish between the two when their differences in frequencies are small (see below). Because of the mass effect, the vibrations of $\text{M}_2\text{X}_6^{2-}$ exhibit the frequency order, $\text{F} > \text{Cl} > \text{Br} > \text{I}$, the same as MX_4^{2-} , as shown in Table 4. When the scaled vibrational frequencies are compared to the measured ones, we find a maximum deviation of $\pm 16 \text{ cm}^{-1}$, except for $B_{3u}\nu_{16}$ of $\text{Pd}_2\text{Cl}_6^{2-}$. It is notable that consistent results between the scaled and the measured frequencies are obtained with the constant scale factor of 1.12.

Table 5 lists a comparison of the vibrational frequencies between the MX_4^{2-} and $\text{M}_2\text{X}_6^{2-}$ species. Similar values of frequencies are observed only for the bridging modes of $\text{M}_2\text{X}_6^{2-}$ ($B_{2u}\nu_{13}$ and $B_{3u}\nu_{17}$) and Raman active modes of MX_4^{2-} (A_{1g} and B_{1g}). The terminal modes of $\text{M}_2\text{X}_6^{2-}$ correspond to the E_u modes of MX_4^{2-} , though, the frequencies of terminal modes of

TABLE 4: Vibrational Frequencies of $\text{M}_2\text{X}_6^{2-}$ (Scaling Factor = 1.12)

| anion | calcd | scaled | exptl ⁴⁰ | assignment |
|-------------------------------|----------|--------|---------------------|--|
| $\text{Pd}_2\text{F}_6^{2-}$ | 234(17) | 262 | | $B_{1u}\nu_9$ out-of-plane deformation |
| | 511(286) | 572 | | $B_{2u}\nu_{12}$ M-X stretching |
| | 384(3) | 430 | | $B_{2u}\nu_{13}$ M-X stretching |
| | 525(226) | 588 | | $B_{3u}\nu_{16}$ M-X stretching |
| | 433(221) | 485 | | $B_{3u}\nu_{17}$ M-X stretching |
| $\text{Pd}_2\text{Cl}_6^{2-}$ | 144(33) | 161 | 156(1) | $B_{1u}\nu_9$ out-of-plane deformation |
| | 315(237) | 353 | 335(10) | $B_{2u}\nu_{12}$ M-X stretching |
| | 238(1) | 267 | 262(sh) | $B_{2u}\nu_{13}$ M-X stretching |
| | 331(142) | 371 | 343(10) | $B_{3u}\nu_{16}$ M-X stretching |
| | 260(47) | 292 | 297(2) | $B_{3u}\nu_{17}$ M-X stretching |
| $\text{Pd}_2\text{Br}_6^{2-}$ | 96(1) | 108 | 113(1) | $B_{1u}\nu_9$ out-of-plane deformation |
| | 232(171) | 260 | 257(10) | $B_{2u}\nu_{12}$ M-X stretching |
| | 151(3) | 169 | 178(0) | $B_{2u}\nu_{13}$ M-X stretching |
| | 248(76) | 278 | 264(8) | $B_{3u}\nu_{16}$ M-X stretching |
| | 168(1) | 188 | 192(0) | $B_{3u}\nu_{17}$ M-X stretching |
| $\text{Pd}_2\text{I}_6^{2-}$ | 74(3) | 83 | | $B_{1u}\nu_9$ out-of-plane deformation |
| | 195(133) | 218 | 218(10) | $B_{2u}\nu_{12}$ M-X stretching |
| | 92(3) | 103 | | $B_{2u}\nu_{13}$ M-X stretching |
| | 208(53) | 233 | 218(10) | $B_{3u}\nu_{16}$ M-X stretching |
| | 125(1) | 140 | 140(sh) | $B_{3u}\nu_{17}$ M-X stretching |
| $\text{Pt}_2\text{F}_6^{2-}$ | 237(43) | 265 | | $B_{1u}\nu_9$ out-of-plane deformation |
| | 528(219) | 591 | | $B_{2u}\nu_{12}$ M-X stretching |
| | 409(38) | 458 | | $B_{2u}\nu_{13}$ M-X stretching |
| | 541(162) | 606 | | $B_{3u}\nu_{16}$ M-X stretching |
| | 436(278) | 488 | | $B_{3u}\nu_{17}$ M-X stretching |
| $\text{Pt}_2\text{Cl}_6^{2-}$ | 143(4) | 157 | 158(1) | $B_{1u}\nu_9$ out-of-plane deformation |
| | 307(0) | 344 | 330(sh) | $B_{2u}\nu_{12}$ M-X stretching |
| | 277(0) | 310 | 300(sh) | $B_{2u}\nu_{13}$ M-X stretching |
| | 316(107) | 354 | 341(10) | $B_{3u}\nu_{16}$ M-X stretching |
| | 268(94) | 300 | 312(5) | $B_{3u}\nu_{17}$ M-X stretching |
| $\text{Pt}_2\text{Br}_6^{2-}$ | 97(4) | 109 | | $B_{1u}\nu_9$ out-of-plane deformation |
| | 209(119) | 235 | 236(10) | $B_{2u}\nu_{12}$ M-X stretching |
| | 166(0) | 186 | 192(0) | $B_{2u}\nu_{13}$ M-X stretching |
| | 220(57) | 247 | 239(sh) | $B_{3u}\nu_{16}$ M-X stretching |
| | 178(3) | 200 | 210(0) | $B_{3u}\nu_{17}$ M-X stretching |
| $\text{Pt}_2\text{I}_6^{2-}$ | 82(1) | 92 | | $B_{1u}\nu_9$ out-of-plane deformation |
| | 171(83) | 192 | 196(10) | $B_{2u}\nu_{12}$ M-X stretching |
| | 125(3) | 140 | 147(1) | $B_{2u}\nu_{13}$ M-X stretching |
| | 178(38) | 200 | 196(10) | $B_{3u}\nu_{16}$ M-X stretching |
| | 135(2) | 151 | 157(3) | $B_{3u}\nu_{17}$ M-X stretching |

TABLE 5: Comparison of Vibrational Frequencies between MX_4^{2-} and $\text{M}_2\text{X}_6^{2-}$

| | $\text{Pd}_2\text{Cl}_6^{2-}$ (PdCl_4^{2-}) | $\text{Pd}_2\text{Br}_6^{2-}$ (PdBr_4^{2-}) | $\text{Pt}_2\text{Cl}_6^{2-}$ (PtCl_4^{2-}) | $\text{Pt}_2\text{Br}_6^{2-}$ (PtBr_4^{2-}) |
|-----------------------------|---|---|---|---|
| $B_{2u}\nu_{13}(B_{1g})$ | 262(270) | | 300(305) | 192(192) |
| $B_{3u}\nu_{17}(A_{1g})$ | 297(300) | | 312(328) | 210(205) |
| $B_{2u}\nu_{12}(\nu_6 E_u)$ | 335(321) | 257(243) | 330(313) | 236(227) |
| $B_{3u}\nu_{16}(\nu_6 E_u)$ | 343(321) | 264(243) | 341(313) | 239(227) |

$\text{M}_2\text{X}_6^{2-}$ are much higher than those of E_u modes of MX_4^{2-} . This result may be due to the existence of a different vibration that has contributions from both terminal and bridging bonds.³⁸

A clear separation of terminal modes from the bridging modes can be achieved only for the stretching modes of $\text{Pt}_2\text{Cl}_6^{2-}$.

Conclusion

This study indicates that the ab initio method performed at the RHF/LANL2DZ level can be applied to the computation of the far-infrared spectra of palladium and platinum halide complexes using a uniform scale factor. The consistency between calculated and measured vibrational frequencies is remarkable. On the bases of our calculations, some fundamental frequencies in the literature need to be reassigned while some vibrational frequencies, such as those of MF_4^{2-} and $\text{M}_2\text{F}_6^{2-}$ can be predicted. Extension of this study to other transition metal halide complexes is underway.

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