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# BOND ENERGIES (Pt—$NH_3$, Pt—Cl) AND PROTON AFFINITY OF CISPLATIN: A DENSITY FUNCTIONAL THEORY APPROACH

**M. Juhász[1], S. Takahashi[1], S. Arulmozhiraja[2], T. Fujii[1]**

[1]*Department of Chemistry, Faculty of Sciences and Engineering, Meisei University, Hino, Tokyo, Japan,* e-mail: fujii@chem.meisei-u.ac.jp
[2]*Research School of Chemistry, Australian National University, Canberra, Australia*

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The energies of the Pt—$NH_3$ and Pt—Cl bonds of cisplatin are calculated by means of a density functional theory method with the B3LYP functional and various basis sets. The calculated bond energies of 37.38 kcal·mol$^{-1}$ and 64.35 kcal·mol$^{-1}$ for Pt—$NH_3$ and Pt—Cl, respectively, agree well with the experimental values (37.28 kcal·mol$^{-1}$ and 69.31 kcal·mol$^{-1}$ respectively) derived from enthalpy changes. The proton and lithium ion affinities of cisplatin are also obtained with the B3LYP functional. Structural characterizations for the protonated and lithiated cisplatin complexes are given. Protonation and lithiation alter the geometric parameters, and the gas-phase proton affinity (198.71 kcal·mol$^{-1}$) is much higher than the lithium ion affinity (70.32 kcal·mol$^{-1}$).

**K e y w o r d s:** *cis*-diamminedichloroplatinum(II), bond strength, cation affinities, B3LYP density functional.

## INTRODUCTION

Cisplatin [*cis*-diamminedichloroplatinum(II)] was the first in a series of square planar platinum(II)-containing chemotherapy drugs and is still one of the most widely and successfully used anticancer agents for the treatment of solid tumor. Because of its importance, cisplatin is still one of the most widely studied drugs in the computational chemistry as well that is indicated by the theoretical studies published recently [ 1—4 ]. In spite of these theoretical studies, the bond energies for Pt—$NH_3$ and for Pt—Cl were not computed in cisplatin.

Besides its pharmaceutical and medical importance, cisplatin and its higher-coordinated complexes are of interest because of their involvement in the field of catalysts. The thermal treatment of transition metal compounds is a widely used method for the preparation of metal catalysts, and platinum catalysts have been produced by the thermal decomposition of cisplatin and a higher-coordination complex [ 5, 6 ].

Both in pharmaceutical research and catalysts, information about the fundamental physical and chemical properties of target molecules, such as their geometrical structure and bond energies, is important. For example, information about the energies of the cisplatin bonds can be expected to provide meaningful information about the chemistry of cisplatin under physiological conditions, which in turn would be useful for designing novel metal-based anticancer agents.

Using microcalorimetry, Skinner et al. [ 7 ] determined the thermal decomposition enthalpy of cisplatin, from which the formation enthalpy could be calculated and the strengths of the Pt-ligand bonds could be deduced [ 8 ]. In this way, the energy of the Pt—Cl bonds in cisplatin was determined to be 69.31 kcal·mol$^{-1}$. Ion-cyclotron studies were made by Kappes and Staley [ 9 ] on gaseous $NiL_2^+$

ions (where L = ammonia, amines, pyridine) and a relative order of $Ni^+$—L bond dissociation energies were established for them. The $Ni^+$-pyridine bond had the highest dissociation energy; $Ni^+$—$NH_3$ bond had the smallest dissociation energy, and between them 5.98 kcal·mol$^{-1}$ difference was found [ 9 ]. Accepting that the same tendency is valid for the bond energies in amine—$PtCl_2$ complexes and using the 69.31 kcal·mol$^{-1}$ determined for Pt—Cl bond, the energy of the Pt—$NH_3$ bond was calculated to be 37.28 kcal·mol$^{-1}$ [ 8 ]. Quantum chemistry methods [ 2, 4, 10—12 ] have been used to study the molecular properties of cisplatin, but the energies of the Pt—Cl and Pt—$NH_3$ bonds have not yet been theoretically computed.

Also, knowledge of a molecule′s proton affinity, which is a fundamental property of the molecule, is required for understanding proton transfer reactions. Proton affinity is a measure of the gas-phase basicity of an anion, neutral atom, or molecule that accepts a proton. The proton affinity of cisplatin has neither been determined experimentally nor been calculated theoretically.

Similarly, the $Li^+$ ion affinity is also an important molecular property. For example, the efficiency of $(M + Li)^+$ ion formation depends strongly on the $Li^+$ ion affinity of a molecule M, which can be as high as approximately 70 kcal·mol$^{-1}$ [ 13—16 ]. Unfortunately, $Li^+$ ion affinities have not yet been reported for many molecules, especially for metal complexes. However, theoretical methods are effective tools for determining accurate ion affinities, which indicate which molecules can be detected at low concentrations as lithiated complexes. For example, the calculated $Li^+$ ion affinity of the transition metal complex Cu(hfac)(tmvs) (50.75 kcal·mol$^{-1}$) is large enough that the ion can been detected by $Li^+$ ion attachment mass spectrometry [ 17 ].

By considering these facts, in the present study we used density functional theory to obtain reliable bond energies for the Pt—Cl and Pt—$NH_3$ bonds of cisplatin and also to study the gas phase reactivity of cisplatin with $H^+$ and $Li^+$ ions.

## COMPUTATIONAL DETAILS

All the computations were performed using Gaussian 03 revision D.01 [ 18 ]. The molecular structures were plotted with the GaussView program [ 19 ]. All the calculations described in this paper were carried out with the B3LYP density functional [ 20—23 ]. We used a variety of basis sets including the split valence-type 6-311+G(*d*,*p*) basis set [ 24, 25 ] for the H, N, and Cl atoms and the Stuttgart/Dresden (SDD) effective core potential (ECP) basis set [ 26, 27 ] for the Pt atom. We optimized the *cis*-$Pt(NH_3)_2Cl_2$ structure using the B3LYP functional with the specified basis sets. We also performed separate optimizations to obtain the structures and total energies of $Pt(NH_3)_2$, $PtCl_2$, $NH_3$, and Cl fragments. We carried out frequency calculations for all the optimized structures to characterize them as minimum energy structures on their respective potential energy surfaces. Bond energies were obtained from the energies of the individual species: $\Delta E[\text{Pt—NH}_3] = 1/2\{E[PtCl_2] + 2E[NH_3] - E[Pt(NH_3)_2Cl_2]\}$, and $\Delta E[\text{Pt—Cl}] = 1/2\{E[Pt(NH_3)_2] + 2E[Cl] - E[Pt(NH_3)_2Cl_2]\}$. Zero-point energies and thermal energy corrections at room temperature were included in the bond energies.

To calculate the $H^+$ and $Li^+$ affinities of cisplatin, we optimized protonated and lithiated cisplatin complexes at the same level of theory described above. Following the geometry optimizations, frequency calculations were carried out, which confirmed that the optimized structures of both the complexes corresponded to true minima on their respective potential energy surfaces, and the frequency calculations yielded the zero-point energies ($\Delta E_{ZPE}$). The interaction energy ($\Delta E_0$) between cisplatin and $H^+$ or $Li^+$ is the difference in energy between the sum of the isolated monomers and the complex. Final $H^+$ and $Li^+$ affinities were calculated from the following equation: $\Delta H_{298K} = \Delta E_0 + \Delta E_{thermal} + \Delta(pV)$, where $\Delta E_{thermal}$ is the thermal energy correction to the room temperature enthalpy, and $\Delta(pV)$ accounts for the translational energy of the cation as well as the $\Delta(nRT)$ term.

## RESULTS AND DISCUSSION

**Bond energies.** The optimized structure and important geometrical parameters of cisplatin are given in Fig. 1 along with the available experimental structural parameters obtained using the X-ray

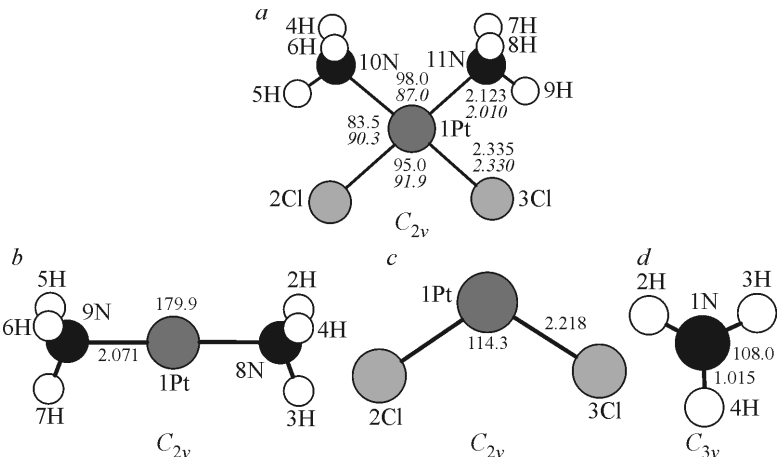


*Fig. 1.* Structures optimized with the B3LYP functional and the combination of the 6-311+G(*d*,*p*) and ECP included SDD basis sets of (*a*) cisplatin, (*b*) $Pt(NH_3)_2$, (*c*) $PtCl_2$, and (*d*) $NH_3$.

Bond lengths are given in Angstroms, and bond angles are in degrees. Literature values [ 28 ] obtained by X-ray crystallographic studies for cisplatin are given in italics

diffraction method [ 28 ]. Also, the optimized structures of $Pt(NH_3)_2$, $PtCl_2$, and $NH_3$ fragments along with their important structural parameters are given in Fig. 1.

The optimized structure of the cisplatin molecule had $C_{2v}$ symmetry, and the symmetry and the geometrical parameters we obtained agreed well with the available theoretical results for the gas phase [ 2, 4 ]. According to the X-ray diffraction study by Milburn et al. [ 28 ], the N—Pt—N, N—Pt—Cl, and Cl—Pt—Cl bond angles are 87.0°, 90.3°, and 91.9° respectively. The corresponding calculated values of 98.0°, 83.5°, and 95.0°, derived in the present study, have some significant differences with the experimental ones (Fig. 1, *a*). A similar discrepancy in the Pt—N and Pt—Cl bond lengths have also been noticed between the theoretically and the experimentally determined values. This phenomenon is not surprising, but is an expected one as the structure of cisplatin in the solid state is different from that in the gas phase. The discrepancy is mainly due to the fact that cisplatin does not behave as an isolated molecule in the solid. The intermolecular interactions existing between the two adjacent cisplatin molecules in the crystal lead to loss of symmetry (has a quasi $C_{2v}$ conformation [ 28 ]) that is different from the gas-phase conformation. The H···H repulsions and the intramolecular N—H···Cl interactions in the gas phase [ 4 ] increase the N—Pt—N and the Cl—Pt—Cl bond angles and decrease both the N—Pt—Cl bond angles compared to those in solid state structure. The intramolecular N—H···Cl interactions present in the gas phase are substituted by intermolecular H bonds in the solid state, which decrease the N—Pt—N bond angle [ 2 ].

Unlike cisplatin, $Pt(NH_3)_2$ has a linear structure (Fig. 1, *b*). The N—Pt—N bond angle in $Pt(NH_3)_2$ is almost double that in cisplatin. In $PtCl_2$ fragment too, the bond angle (Cl—Pt—Cl) is larger than in the parent cisplatin molecule. The N—Pt and Cl—Pt bond lengths in the fragments on the other hand are decreased from those in the cisplatin complex. These differences in the geometries indicate that the same ligands can coordinate differently to the Pt center in $Pt(NH_3)_2$ and $PtCl_2$ than in the cisplatin complex. In $NH_3$, all the N—H bonds are similar (1.015 Å) and all the three H—N—H bond angles are equal (108.0°). However, it is not the case in the cisplatin complex (Fig. 1, *a* and *d*).

The Pt—Cl and Pt—$NH_3$ bond energies in cisplatin calculated with the various basis sets are listed in Table 1 along with the experimental values reported in the literature [ 8 ]. As expected, the calculated Pt—Cl bond energy was higher than the calculated Pt—$NH_3$ bond energy, regardless of which basis set was used, and it was consistent with the literature bond energies.

T a b l e 1

*Calculated bond energies* ($\Delta E$, kcal·mol$^{-1}$) *at* 298.15 K

| Method | $\Delta E$[Pt—$NH_3$] | $\Delta E$[Pt—Cl] |
|---|---|---|
| SDD [a] | 46.96 | 63.02 |
| 6-31+G(*d*) + SDD [b] | 38.86 | 64.32 |
| 6-311+G(*d*,*p*) + SDD [b] | 37.38 | 64.35 |
| Experimental values from Ref.8. | 37.28 | 69.31 |

[a] SDD ECP basis sets for all atoms.

[b] 6-31+G(*d*) or 6-311+G(*d*,*p*) basis set for nonmetal atoms; SDD ECP basis set for Pt.

These results confirm that the covalent Pt—Cl bond is stronger than the dative Pt—$NH_3$ bond.

The calculated bond energies (Table 1) correlate well with the experimentally derived bond energies: the calculated Pt—$NH_3$ bond energy (37.38 kcal·mol$^{-1}$) was almost equal to the experimental value (37.28 kcal·mol$^{-1}$), and the calculated Pt—Cl bond energy was approximately 5 kcal·mol$^{-1}$ smaller than the experimental value. These results show that reliable bond energies could be derived by using a triple-zeta basis set augmented with polarization functions and diffuse functions for heavy atoms and augmented with the SDD ECP basis set for the Pt atom.

Because pyrolysis is initiated by bond breakage, the experimentally determined energy of decomposition (apparent activation energy, $E_a$) of cisplatin into $PtCl_2$ and $NH_3$ can be expected to be associated with the energy of the Pt—$NH_3$ bond. Recently, Fujii studied [ 29 ] the temperature-programmed decomposition of cisplatin by means of infrared image furnace-ion attachment mass spectrometry. The slope of the plot of $NH_3$ signal intensity versus temperature for cisplatin decomposition from 225 to 249 °C was used to determine an $E_a$ value of 38.0 kcal·mol$^{-1}$ for the decomposition of cisplatin into $NH_3$ and $PtCl_2$. This value is in good agreement with the bond energy for Pt—$NH_3$ calculated in the present study.

It is noticed that the Pt—Cl bond energy calculated at 0 K was slightly higher by around 0.13 kcal than that calculated at 298.15 K. This is understandable, as at 0 K, all molecules (*cis*-$Pt(NH_3)_2Cl_2$, $Pt(NH_3)_2$, $PtCl_2$, $NH_3$, and Cl fragments) are in their lowest rotational and vibrational states and therefore, the energy stored in the Pt—Cl chemical bond is higher at 0 K than at 298.15 K. However, the Pt—$NH_3$ bond energy calculations show an opposite trend; Pt—$NH_3$ bond energy is smaller by around 0.38 kcal at 0 K than at 298.15 K. This may be the result of the dative character of the Pt—$NH_3$ bond, but no exact explanation for this discrepancy can be made at this time.

**Proton affinity and $Li^+$ ion affinity.** Starting from the global energy minimum structure of cisplatin (Fig. 1, *a*), we searched the possible sites in the cisplatin molecule for the formation of $H^+$ and $Li^+$ adducts. The possible structures of the complexes were optimized, and then frequency calculations were used to find the global energy minimum structures for both complexes (Fig. 2, *a* and *b*).

As shown in the figures, the protonated and lithiated cisplatin complexes had different structures. The Cl atoms in the cisplatin molecule are the most basic center not only for proton attachment but also for $Li^+$ ion association. In the protonated complex, $H^+$ was connected to one of the Cl atoms, which resulted in a 60° rotation of the amine group from its orientation in the cisplatin monomer; the orientation of the other amine group was unchanged. Rotation of the Pt—N bond reduced the strain due to the attached $H^+$. In the lithiated cisplatin, both Cl atoms interacted with the $Li^+$ ion symmetrically, as evidenced by the equal Cl—Li bond lengths (2.249 Å) and Li—Cl—Pt bond angles (85.3°). Therefore, the $Li^+$ complex retained the $C_{2v}$ symmetry, whereas protonated cisplatin had $C_s$ symmetry.

Protonation at the Pt metal center was also investigated. The obtained structure has a similar cisplatin structure but with $C_s$ symmetry with a newly formed Pt—$H^+$ bond. Energetically, this structure was less stable than the above-mentioned global minima (Fig. 2, *a*) by 85.67 kcal·mol$^{-1}$. Likewise, lithiation at the Pt metal site was also studied, but we did not find any Pt-bond lithiated complex.

As expected, the newly formed ion–ligand bonds in true minima of the complexes (Figs. 2, *a* and *b*) had different bonding natures, as indicated by their geometrical parameters and ion affinities. In the protonated complex, the Pt1—Cl3 and Pt1—N11 bonds were elongated (2.430 Å) relative to the corresponding bonds in cisplatin, whereas the Pt1—Cl2 and Pt1—N10 bonds were shorter (2.317 Å and 2.066 Å respectively). The lengthening of Pt1—Cl3 and Pt1—N11 bonds indicates that electron density is shifted through the N11—Pt1 and Pt1—Cl3 bonds towards $H^+$.

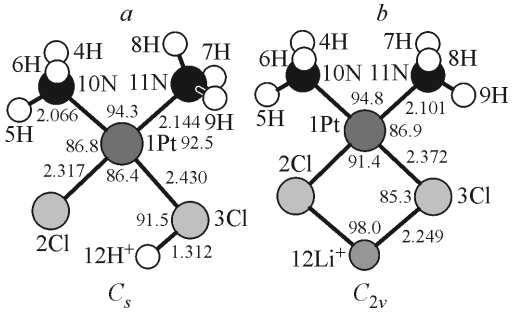


*Fig. 2.* Cisplatin complex structures optimized with the B3LYP functional and the combination of the 6-311+G(*d,p*) and ECP included SDD basis sets: (*a*) protonated cisplatin and (*b*) lithiated cisplatin.
Bond lengths are given in Angstroms, and bond angles are in degrees

Due to the aforementioned 60° rotation of the $NH_3$ group occurred in the protonated complex, H···H repulsions are less pronounced forcing the closure of the N10—Pt1—N11 bond angle and increasing both the Cl2—Pt1—N10 and Cl3—Pt1—N11 bond angles. Like in the Cl3—Pt1—N11 bond angle, a large change was also observed in the Cl2—Pt1—Cl3 bond angle. While the Cl3—Pt1—N11 bond angle increased, the Cl2—Pt1—Cl3 bond angle significantly decreased. The large changes observed in these bonds are due to the attached $H^+$, which may be somehow better attracted by Cl2 than by completely saturated N11. In the $Li^+$ complex, the Pt—Cl bonds were longer (2.372 Å), and the Cl—Pt—Cl bond angle was markedly smaller (91.4°), owing to charge transfer; the charge difference of 0.3 (obtained from the calculated Mulliken charges) between cisplatin and the $Li^+$ complex indicates that electron density moved from cisplatin to $Li^+$. As a result, the Pt—$NH_3$ bond lengths were slightly shorter (2.101 Å). All these changes indicate that $H^+$ and $Li^+$ ions interacted strongly with the chloride ligand.

Table 2

*Cation affinities* (kcal·mol$^{-1}$) *calculated with the* B3LYP *functional and various basis sets*

| Basis set | Proton affinity | Lithium ion affinity |
|---|---|---|
| SDD [a] | 188.83 | 69.09 |
| 6-31+G(*d*) + SDD [b] | 195.48 | 69.08 |
| 6-311+G(*d*,*p*) + SDD [b] | 198.71 | 70.32 |

[a] The SDD ECP basis set was used for all atoms.

[b] The 6-31+G(*d*) or 6-311+G(*d*,*p*) basis set was used for nonmetal atoms; the SDD ECP basis set was used for Pt.

Because $H^+$ is a harder Lewis acid than $Li^+$, the interaction between cisplatin and $H^+$ was expected to be stronger than that between cisplatin and $Li^+$. The affinity data in Table 2 strongly support this assumption. The cisplatin-cation distance was shorter for $H^+$ (1.312 Å) than for $Li^+$ (2.249 Å), which is understandable because the radius of $H^+$ is smaller than that of $Li^+$. The shorter distance also contributed to the formation of a stronger interaction between cisplatin and $H^+$.

It is important to be mentioned here that the protonated cisplatin complex can exist exclusively in the gas phase. Bonding of $H^+$ to Cl implies that HCl will dissociate in solution and it will be substituted by a water molecule. As it is known, under physiological conditions, both Cl are replaced by water molecules, and results *cis*-$[Pt(NH_3)_2(H_2O)_2]^{2+}$ that be thought as an anticancer form of cisplatin. Also, the lithiated cisplatin complex might appear exclusively in the gas phase. It is not expected to be found in an aqueous solution, because the addition of some water molecules to the coordinated $Li^+$ ion produces the hydrogen bonded structure of cisplatin to the hydrated $Li^+$ ion.

The large affinities of proton and $Li^+$ ion for cisplatin in the gas phase indicate that these ions are strongly bound to cisplatin, which may be noteworthy among physical and synthetic chemists. The proton affinity of 198.71 kcal·mol$^{-1}$ indicates that protonated cisplatin could be observed easily by means of chemical ionization—mass spectrometry. In addition, under electrospray ionization—mass spectrometry conditions, the high proton affinity can be expected to contribute to the easier detection of cisplatin samples because protonated cisplatin adducts would form readily. The large $Li^+$ ion affinity calculated for cisplatin indicates that cisplatin can be expected to react easily with $Li^+$ ions in the gas phase and hence, be detected and quantified by Li ion attachment mass spectrometry.

## CONCLUSIONS

We performed the first density functional theory calculations of the Pt—$NH_3$ and Pt—Cl bond energies in cisplatin, along with its $H^+$ and $Li^+$ ion affinities. The bond energies calculated with the B3LYP functional and various basis sets were considerably smaller for Pt—$NH_3$ than for Pt—Cl. The calculated bond energies were well comparable to the experimental values. Our results confirm that the Pt—Cl bond is stronger than the Pt—$NH_3$ bond in cisplatin. The calculated $H^+$ and $Li^+$ affinities of cisplatin were large. The large $H^+$ and $Li^+$ affinities indicate that chemical ionization mass spectrometry and ion attachment mass spectrometry could be used to detect cisplatin in the gas phase.

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