Assessment of new DFT methods for predicting vibrational spectra and structure of cisplatin: Which density functional should we choose for studying platinum(II) complexes?

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HIGHLIGHTS

- New DFT methods are assessed for theoretical study of platinum(II) complexes.
- LC-ωPBE is superior to other functionals in predicting the structure of cisplatin.
- PBE0 and mPW1PW are recommended for calculations of vibrational spectra of Pt(II) complexes.
- LanL2TZ(f) basis set for Pt improves the accuracy of the theoretical results.

GRAPHICAL ABSTRACT

ARTICLE INFO

ABSTRACT

Ten different DFT methods, including several recently developed functionals have been tested for their performances in prediction of infrared and Raman spectra and molecular structure of cisplatin. The assessed DFT methods cover the range from meta-GGA to hybrid, double hybrid and long-range corrected hybrid models (M06-L, M06, M06-2X, PBE0, mPW1PW, B3LYP, B2PLYP, CAM-B3LYP, ωB97XD and LC-ωPBE). The calculated structural parameters and theoretical spectra have been compared to the corresponding experimental data. It is shown that the LC-ωPBE scheme is superior to other DFT methods in predicting the geometry of cisplatin. Unfortunately, the M06-L, M06-2X and B3LYP functionals are deficient in the evaluation of the strength of two Pt $\leftarrow$ NH$_3$ coordination bonds in cisplatin (the calculated bond lengths are too long and the Pt–N stretching frequencies are underestimated). Both the PBE0 and mPW1PW functionals, in conjunction with the LanL2TZ(f) basis set for Pt give very similar theoretical results and seem to be the best methods for predicting the IR and Raman spectra of cisplatin. The long-range corrected functionals (LC-ωPBE, ωB97XD and CAM-B3LYP) have shown good performances in predicting the frequencies of Pt-ligand vibrations and are promising new tools for theoretical study of novel platinum(II) compounds.

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Introduction

The discovery of the antitumor properties of cisplatin, cis-diamminedichloroplatinum(II), by Rosenberg et al. [1] was a cornerstone for the era of platinum-based anticancer chemotherapy. When clinical tests with cisplatin began in 1972, diagnosis of a testicular cancer usually meant a death sentence [2]. Today, this type of cancer treated with cisplatin or carboplatin has a cure rate approaching 100% [2,3]. Cisplatin has become an important component in chemotherapy of ovarian, testicular and bladder cancers, as well as in the treatment of lymphomas and myelomas.

Unfortunately, efficacy of cisplatin has been greatly hampered by severe dose limiting side effects including nephrotoxicity, neurotoxicity and ototoxicity [4]. Many tumors display inherent resistance to cisplatin, while others develop acquired resistance after initial treatment [5,6]. Over the last 40 years, thousands of platinum compounds have been prepared and screened as potential antitumor agents [7–9]. As a result of these efforts the five new anticancer drugs: carboplatin, oxaliplatin, nedaplatin, lobaplatin, and heptaplatin have entered the clinical therapy. The two of them, carboplatin, [*cis*-diammine(1,1-cyclobutanedi-carboxylato)platinum(II)] [10] and oxaliplatin, [(1*R*,2*R*-cyclohexanediamine) oxalatoplatinum(II)] [11] have been approved as anticancer drugs throughout the world. The other three drugs have gained regional approval: nedaplatin, *cis*-diammine(hydroxyacetato) platinum(II)] in Japan [12]; lobaplatin, [2-hydroxy-propanoato(1,2-cyclobutane dimethanamine)platinum(II)] in China [13] and heptaplatin, propanedioato[2-(1-methylethyl)-1,3-dioxolane-4,5-dimethanamine)platinum(II)] in South Korea [14].

Currently, approximately 50% of all the cancer patients receive a platinum compound. To improve clinical effectiveness of the platinum-based chemotherapy, continuing search for the novel platinum drugs is inevitable. Some platinum agents (including picoplatin and satraplatin) are undergoing clinical trials [7,8]. Several newly synthesized Pt(II) complexes have revealed a high anticancer activity *in vitro* as compared to cisplatin [15–17].

In the case when the structure of a new platinum(II) complex cannot be determined by a single crystal X-ray diffraction analysis, the calculations of the molecular geometry and vibrational spectra by quantum chemistry methods, combined with experimental studies of the Raman and IR spectra of the Pt(II) complex play an important role in the elucidation of its structure. Moreover, the calculations of vibrational frequencies and IR/Raman intensities accompanied by normal coordinate analysis are indispensible in making the reliable assignments of the experimental vibrational spectra.

In our earlier work [18], we have demonstrated that the mPW1PW density functional [19] is remarkably superior to MP2, HF and all the remaining DFT methods (including B3LYP) in a simultaneous prediction of the molecular structure and vibrational frequencies of cisplatin and carboplatin. In the other our studies on different platinum complexes [20–22] we have shown that the theoretical Raman and IR spectra calculated by the mPW1PW functional are in good agreement with the experimental spectra.

Several other groups also examined various theoretical approaches for the prediction of the molecular properties of cisplatin [23–28].

In the past decade, much progress has been made in the design of new DFT methods, which have been implemented into available quantum chemical computational programs. Among the new methods is the M06 family of functionals (M06-L, M06, M06-2X), the long-range corrected hybrid models (CAM-B3LYP, ωB97XD and LC-ωPBE) and the double hybrid functionals (e.g. B2-PLYP).

The aim of the present work is to address the following questions:

how well can these new DFT methods predict the structural parameters and vibrational spectra of cisplatin? and,
which density functional should we choose for studying new platinum anticancer agents?

We have evaluated the performance of the above-mentioned new functionals, and compared the results with those obtained by the other DFT methods (B3LYP, mPW1PW and PBE0) for cisplatin).

Methods

Experimental

Cisplatin (*cis*-[PtCl$_2$(NH$_3$)$_2$]) was purchased from Sigma Chemical Co.

The Fourier transform far infrared (FT-FIR) and middle-infrared (FT-IR) spectra were measured on a Bruker VERTEX 70 V vacuum spectrometer equipped with an ATR accessory and air-cooled DTGS detector. The FT-IR spectra (in the range 4000–400 cm^{-1}) were recorded in KBr pellets. For the far IR spectra (in the range 600–50 cm^{-1}) the diamond ATR accessory was used and the spectra were elaborated in the OPUS™ software to convert them from reflectance into absorbance. The instrument was kept under vacuum during the measurements, and the spectra were recorded at a resolution of 2 cm^{-1}.

The FT-Raman spectra (in the range 3500–50 cm^{-1}) were measured on a Bruker MultiRAM spectrometer equipped with a Nd:YAG laser (emitting radiation at a wavelength of 1064 nm) and a liquid nitrogen cooled germanium detector. The spectra were recorded at a resolution of 2 cm^{-1} with co-addition of 256 scans.

Theoretical

The optimized geometry, vibrational frequencies, IR intensities and Raman scattering activities of cisplatin were calculated by 10 density functional methods. The tested functionals include new DFT methods, and cover the range from local meta-GGA (meta-generalized gradient approximation) to hybrid, double hybrid and long-range corrected hybrid functionals.

Among the Minnesota M06-class of density functionals we have used the following methods: M06-L, M06 and M06-2X. The M06-L functional [29] is a local meta-GGA protocol (meta-GGA means that it depends not only on spin density and its reduced gradient, but also on spin kinetic energy density). This functional was recommended for calculations of bond lengths and vibrational frequencies of large systems containing transition metals [29]. The M06 and M06-2X methods are the hybrid meta-GGA functionals, where the Hartree–Fock exchange energy (X) is equal to 27% and 54%, respectively (2X means double the amount of nonlocal exchange energy) [30]. The M06 functional was parametrized including transition metals and nonmetals, while the M06-2X was parametrized only for nonmetals.

The three long-range corrected hybrid functionals (CAM-B3LYP, ωB97XD and LC-ωPBE) were employed in this study. CAM-B3LYP [31] is a new hybrid exchange–correlation functional using the Coulomb attenuating method (this is the long-range corrected version of the B3LYP functional). The ωB97XD method [32] comprises a modified B97 exchange and correlation functionals, and also includes the long-range correction with empirical atom–atom empirical dispersion (D). LC-ωPBE [33] is the long-range corrected version of hybrid ωPBE functional. Unfortunately, no Raman intensities are available for LC-ωPBE, because calculations of polarizability derivatives for this functional have not been implemented in the Gaussian 09 package.

In addition, we have used the double hybrid B2-PLYP functional [34] representing a new generation of DFT methods, which is based on the MP2 calculation of a long-range correlation energy. B2-PLYP is a (27, 53) double hybrid which means that it includes 27% of the MP2-type correlation and 53% of the Hartree–Fock exchange energy [34].

For comparison, all calculations were also performed with the B3LYP, mPW1PW and PBE0 density functional methods. B3LYP is the widely used three-parameter hybrid GGA functional [35–37]. The mPW1PW protocol (mPW1PW91) [19] is the Becke-style