Trichloro(dinitrogen)platinate(II)

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Abstract

Zeise's salt, $[PtCl_3(H_2C=CH_2)]^-$, is the oldest known organometallic complex, featuring ethylene strongly bound to a platinum salt. Many derivatives are known, but none involving dinitrogen, and indeed dinitrogen complexes are unknown for both platinum and palladium. Electrospray ionization mass spectrometry of $K_2[PtCl_4]$ solutions generate strong ions corresponding to $[PtCl_3(N_2)]^-$, whose identity was confirmed through ion mobility spectroscopy and MS/MS experiments that proved it to be distinct from its isobaric counterparts $[PtCl_3(C_2H_4)]^-$ and $[PtCl_3(CO)]^-$. Computational analysis established a gas-phase platinum-dinitrogen bond strength of 116 kJ mol^{-1}, substantially weaker than the ethylene and carbon monoxide analogues but stronger than for polar solvents such as water, methanol and dimethylformamide, and strong enough that the calculated N-N bond length of 1.119 Å represents weakening to a degree typical of isolated dinitrogen complexes.

Graphical abstract
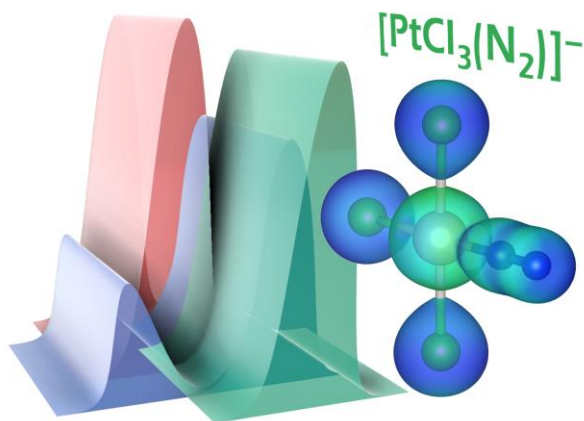
The dinitrogen analogue of Zeise's salt, $[PtCl_3(N_2)]^-$, is readily formed in the gas phase, can be easily distinguished from its isobaric counterparts and has a calculated bond strength commensurate with isolated dinitrogen complexes despite such complexes of platinum being unknown.

Keywords

Zeise's salt, [PtCl$_3$(H$_2$C=CH$_2$)]$^-$, is the oldest known organometallic complex and was originally met with some criticism.[1] It was made by Zeise in 1830 by boiling platinum tetrachloride in ethanol and isolating a salt he called "entzündliches Kali-Platin-Salz" (flammable potassium platinum salt), noting that it had a long-lasting metallic flavor.[2] Zeise's salt was later prepared by Birbaum using ethylene,[3] and eventually its structure was determined crystallographically.[4,5] The ethylene binds side-on, in a bonding mode described by the Dewar-Chatt-Duncanson model.[6–10] Zeise's salt inspired generations of research into organometallic chemistry, and numerous derivatives have been prepared with a variety of 2-electron ligands replacing ethylene.[11–15]

Because the ethylene ligand binds tenaciously to the platinum, we were interested to see if it would remain bound even during the desolvation process during electrospray ionization mass spectrometry (ESI-MS). Monodentate alkenes tend to bind weakly to metal centers, and it is generally difficult to preserve their coordination even under the mildest of ESI-MS conditions.[16,17] Zeise's salt can be readily prepared via SnCl$_2$-catalyzed ligand substitution of [PtCl$_4$]$^{2-}$ with ethylene,[18] and substitution of Cl for heavier halides has been explored.[19,20] When we examined a [PtCl$_4$]$^{2-}$ solution in water a relatively minor peak at the correct m/z and with the expected isotope pattern for [PtCl$_3$(C$_2$H$_4$)]$^-$ was observed, despite the absence of ethylene. That ion could be subjected to collision-induced dissociation (CID) in a conventional product ion MS/MS experiment, and it readily lost a neutral species of 28 Da. Nitrogen, like ethylene, also has a molecular weight of 28 Da, and is present in abundance during the ESI-MS experiment thanks to its use as a desolvation gas, and was a possible explanation for this ion. While many dinitrogen complexes have been reported for metal centers in Group 3-9, some simple,[21–25] some with carefully constructed coordination environments,[26–34] and others evolved for the purpose,[35–39] such complexes are less common in Group 10 and 11. Isolated dinitrogen complexes involving platinum are unknown. Pt–N$_2$ bonds have been studied under specialized conditions using infrared spectroscopy, laser ablation, and matrix isolation.[40–43] A few ions observed mass spectrometrically have been tentatively assigned to platinum dinitrogen species, including [Pt(NH$_3$)$_2$(N$_2$)Cl]$^+$[44] and [Pt(NH$_3$)$_2$(N$_2$)OH]$^+$.[45] [PtCl$_3$N$_2$]$^-$ ions were assigned in the experimental section of a study on bicyclic antitumor platinum(IV) complexes,[46] but escaped without comment in the manuscript. Interest in dinitrogen complexes has been long-standing due to the inherent difficulty of activating the very strong dinitrogen bond, a prerequisite for involving the molecule in catalytic processes.[47]

We provide detailed evidence for the robustness of gas-phase [PtCl$_3$(N$_2$)]$^-$ using a multi-faceted approach: accurate mass analysis, MS/MS studies, ion mobility spectroscopy (IMS), and computational chemistry. We compared all molecules of mass 28 Da that can act as a ligand for the [PtCl$_3$]$^-$ fragment:

ethylene, dinitrogen, and carbon monoxide. The resulting [PtCl3(L)]⁻ complexes are numbered **1** (L = C2H4), **2** (L = N2) and **3** (L = CO).

NEt4(PtCl3(CO)) and K(PtCl3(C2H4)) complexes were synthesized (see ESI) for direct comparison to the suspected [PtCl3(N2)]⁻ complex. Accurate mass data were collected on a Synapt G2-Si instrument for all species (Figure 1). These data clearly depict the distinct differences in exact mass for each of these complexes, and provide strong evidence of the authenticity of the N2 complex **2**. An overlaid plot of the full experimental isotope pattern and theoretical isotope pattern can be found in the Supporting Information (Figure S1).
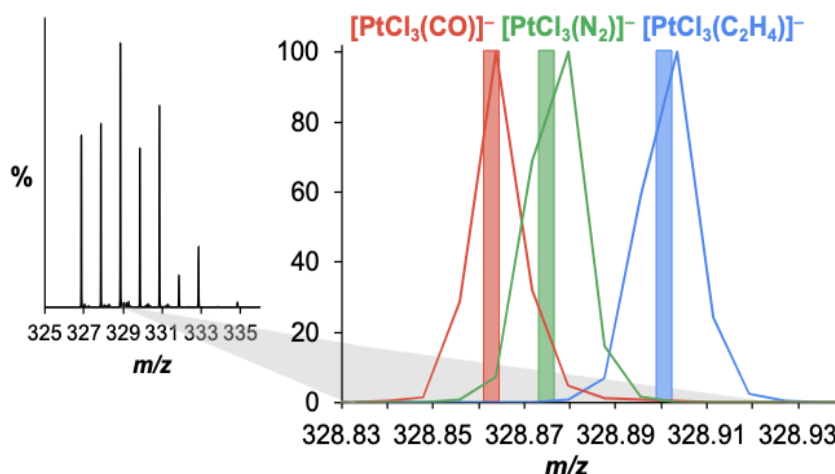

Figure 1. Overlaid plot of theoretical peak position (bar width = 10 ppm) and experimental data for [PtCl3(C2H4)]⁻ (**1**, blue), [PtCl3(N2)]⁻ (**2**, green), and [PtCl3(CO)]⁻ (**3**, red).

Modern mass spectrometers are capable of collecting corroborating data on the identity of ions that have the same nominal mass. Fragmentation via collision-induced dissociation produces diagnostic product ions based on the strength of the bonds.[48–51] In the case of organometallic compounds, weakly bound ligands will dissociate at a lower collision energy compared to more strongly bound ligands. The product ion scans reveal a loss of *m/z* 28, meaning that the Cl⁻ ligands remain bound while the L ligand dissociates; for Zeise's salt this is the ethylene ligand. MS/MS experiments on each of **1**, **2** and **3** showed clear differences in terms of how difficult it is to remove each ligand (Figure 2). The N2 ligand is the most weakly bound as its relative intensity was reduced to 50% of its initial intensity at a collision energy of just 2.7 V. The CO ligand is strongly bound to the Pt centre, and requires a much higher collision energy to dissociate; 13.1 V was required to reduce this complex to 50% of its initial intensity. The binding strength of the ethylene ligand of Zeise's salt falls in between that of N2 and CO, requiring a collision energy of 10.3 V to produce the same degree of dissociation.
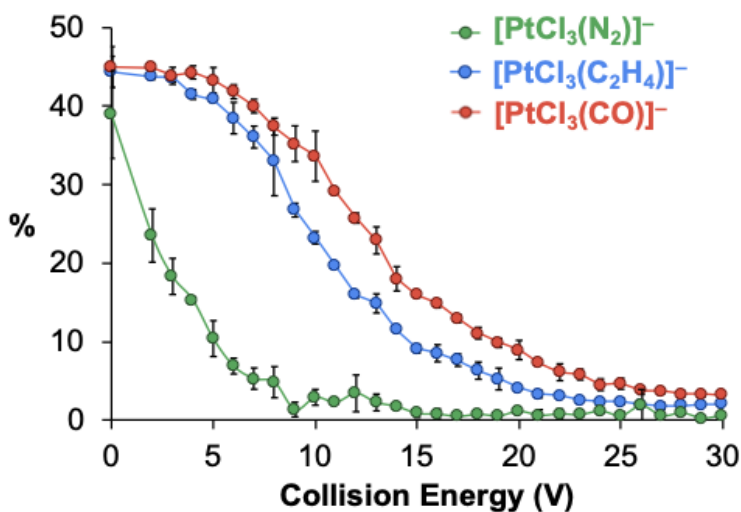
Figure 2. MS/MS data obtained for $[PtCl_3(C_2H_4)]^-$ (blue), $[PtCl_3(N_2)]^-$ (green) and $[PtCl_3(CO)]^-$ (red) showing loss of $[PtCl_3(L)]^-$ as L is removed. Collision energy at 50% of initial relative abundance: $[PtCl_3(N_2)]^- = 2.7$ V, $[PtCl_3(C_2H_4)]^- = 10.3$ V, $[PtCl_3(CO)]^- = 13.1$ V.

Ion mobility data for each of the three complexes was collected on a Waters Synapt G2-Si instrument (Figure 3). Two peaks for **1** arise because the source and flight tube are filled with N_2 and some displacement of ethylene by dinitrogen occurs, thus resulting in ion mobility signals for a mixture of **1** and the dinitrogen complex **2**. The singular peak for **3** suggests little or no displacement of the carbonyl ligand by N_2, in keeping with its greater tenaciousness as a ligand. The difference in drift time for **3** and **1** is somewhat surprising, given the similarities in size of the two complexes (same nominal mass and number of atoms), but drift times are dependent on factors including ion-neutral interactions,[52] drift gas polarizability,[53,54] shape,[55] and charge state.[56] Additionally, ions with a more delocalized charge are less prone to forming short-lived heterodimers with the drift gas molecules.[57–59] Because CO is more highly polarized than N_2 (see Figure 3 insets of electrostatic potentials mapped on to the electron density isosurface) it exhibits a longer drift time despite their similarity in collisional cross-section.
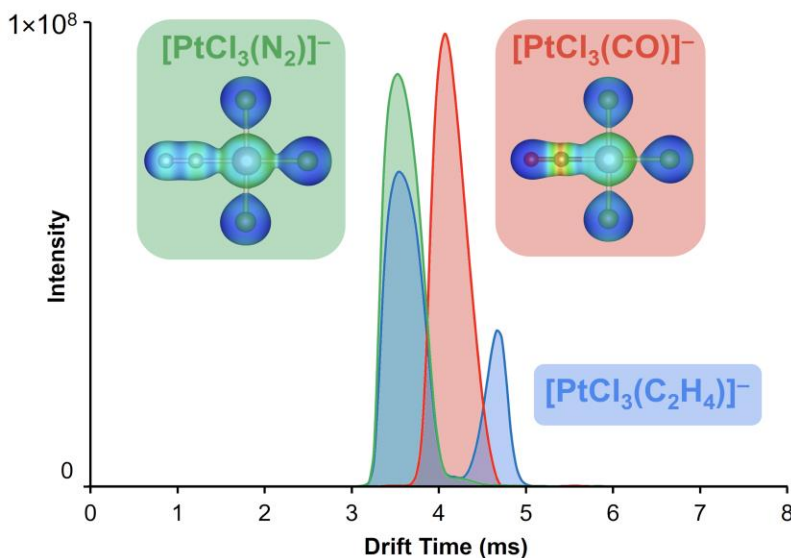
Figure 3. Ion mobility spectrum for [PtCl$_3$(C$_2$H$_4$)]$^-$ (blue), [PtCl$_3$(N$_2$)]$^-$ (green) and [PtCl$_3$(CO)]$^-$ (red); the area of each trace has been normalized to the same value. Structures of [PtCl$_3$(N$_2$)]$^-$ (left) and [PtCl$_3$(CO)]$^-$ (right) show the electrostatic potential (red = 0.8, blue = 0.1) calculated with the orca_vpot keyword and plotted as a cube file[60] mapped onto the electron density isosurface (0.1$e\,Å^{-3}$).

Computational analysis of the three ions allows us to assess the strength of binding of the ligands in the gas phase, and in keeping with the tandem mass spectrometric results, the calculations showed the order of binding strength was CO > C$_2$H$_4$ > N$_2$. Because of the low number of atoms, calculations could be performed at a high level. Binding energies of N$_2$, CO, and C$_2$H$_4$ to [PtCl$_3$]$^-$ were calculated using density functional theory (DFT) at the RI-UB2PLYP/def2-TZVPP level of theory,[61] with D3 dispersion corrections[62] using ORCA 4.0 software.[63] The results predict the strongest bond energies for CO, then ethylene, then dinitrogen, fully supporting the MS/MS (Figure 2) and ion mobility results (Figure 3).
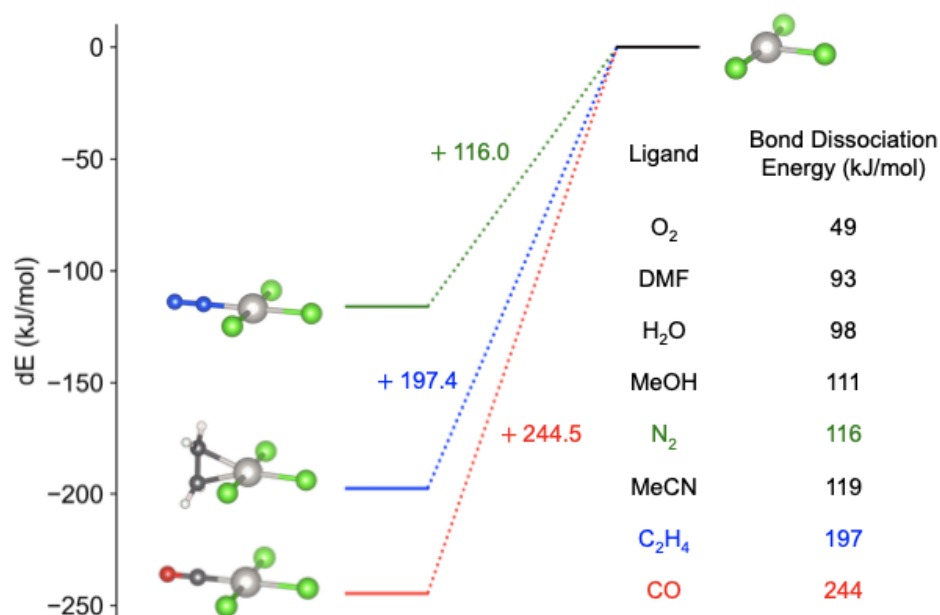
Figure 4: Ligand dissociation energies (LDE) calculated as reaction enthalpies for the dissociation reaction $PtCl_3\text{-}L \rightarrow PtCl_3 + L$. Comparison of C_2H_4, N_2 and CO (diagram) to that of common readily available compounds (table). See supporting information for structures of all other ligands in the table.

The ligand dissociation energies for L ligands in complexes **1**, **2**, and **3** were compared to solvent molecules and O_2 for context (Figure 4 and supporting information). N_2 was found to be a slightly better ligand than methanol and slightly worse than acetonitrile. Other polar ligands examined were water and dimethylformamide (DMF), and these both have markedly lower binding energies than N_2. Dioxygen was the weakest binder of all, with less than half the binding strength of N_2 (unlike N_2, the strongest binding mode for O_2 was side-on rather than end-on).

Frontier molecular orbitals were examined for **1**, **2** and **3** (see Supporting Information). All exhibited the synergistic π back-bonding that is a feature of all three ligands, with filled ligand orbitals σ-donating into empty metal orbitals of appropriate symmetry, and filled metal orbitals donating π electron density back to the ligand into empty π* orbitals.[64–66]

Comparing the calculated N_2 bond length of 1.112 Å in **2** to established bond lengths in structuraly characterized dinitrogen complexes is instructive. Examination of iridium (the closest analogue to Pt) complexes of dinitrogen in the Cambridge Structural Database (36 unique bond lengths are known), we find the N_2 distance falls in the range 0.982 Å[67] to 1.183 Å,[68] with an average of 1.117 Å, strikingly close to that calculated for **2**. The bond length in **2** is most similar to that in an iridium pincer complex prepared by Brookhart and coworkers in which the dinitrogen ligand (N-N distance 1.119 Å) is bound to two iridium

centers.[69]

Given the surprisingly high gas-phase and calculated stability of this platinum dinitrogen complex, **2** makes for an attractive synthetic target as N_2. The relatively high strength of binding may provide exploitable levels of activation of the dinitrogen molecule in water, leading to new opportunities in functionalization and catalysis.

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