

Mass Spectrometry

Trichloro(Dinitrogen)Platinate(II)**

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Abstract: Zeise's salt, $[\text{PtCl}_3(\text{H}_2\text{C}=\text{CH}_2)]^-$, 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 $\text{K}_2[\text{PtCl}_4]$ solutions generate strong ions corresponding to $[\text{PtCl}_3(\text{N}_2)]^-$, the identity of which was confirmed through ion-mobility spectrometry and MS/MS experiments that proved it to be distinct from its isobaric counterparts $[\text{PtCl}_3(\text{C}_2\text{H}_4)]^-$ and $[\text{PtCl}_3(\text{CO})]^-$. 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 \AA represents weakening to a degree typical of isolated dinitrogen complexes.

Zeise's salt, $[\text{PtCl}_3(\text{H}_2\text{C}=\text{CH}_2)]^-$, 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 $[\text{PtCl}_4]^{2-}$ with ethylene,^[18] and substitution of Cl for heavier halides has been explored.^[19,20] When we examined a $[\text{PtCl}_4]^{2-}$ solution in water a relatively minor peak at the correct m/z and with the expected isotope pattern for $[\text{PtCl}_3(\text{C}_2\text{H}_4)]^-$ 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 Groups 3–9, some simple,^[21–25] some with carefully constructed coordination environments,^[26–34] and others evolved for nitrogen fixation,^[35–39] such complexes are less common in Groups 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 $[\text{Pt}(\text{NH}_3)_2(\text{N}_2)\text{Cl}]^{+}$ ^[44] and $[\text{Pt}(\text{NH}_3)_2(\text{N}_2)\text{OH}]^{+}$.^[45] Schwarz and co-workers reported phenanthroline complexes of several transition metals, including Pt, forming an adduct with N_2 buffer gas inside the spectrometer.^[46] $[\text{PtCl}_3\text{N}_2]^-$ ions were assigned in the experimental section of a study on bicyclic antitumor platinum(IV) complexes,^[47] but escaped without comment in the manuscript. Interest in dinitrogen complexes has been longstanding due to the inherent difficulty of activating the very strong dinitrogen bond, a prerequisite for involving the molecule in catalytic processes.^[48]

We provide detailed evidence for the robustness of gas-phase $[\text{PtCl}_3(\text{N}_2)]^-$ using a multifaceted approach: accurate mass analysis, MS/MS studies, ion-mobility spectrometry (IMS), and computational chemistry. We compared all molecules of mass 28 Da that can act as a ligand for the $[\text{PtCl}_3]^-$ fragment: ethylene, dinitrogen, and carbon monoxide. The resulting $[\text{PtCl}_3(\text{L})]^-$ complexes are numbered 1 ($\text{L} = \text{C}_2\text{H}_4$), 2 ($\text{L} = \text{N}_2$) and 3 ($\text{L} = \text{CO}$).

$\text{NEt}_4[\text{PtCl}_3(\text{CO})]$ and $\text{K}[\text{PtCl}_3(\text{C}_2\text{H}_4)]$ complexes were synthesized (see the Supporting Information) for direct comparison to the suspected $[\text{PtCl}_3(\text{N}_2)]^-$ complex. Accurate mass data were collected on a Synapt G2-Si instrument for all species. As shown in Figure 1, $[\text{PtCl}_3(\text{C}_2\text{H}_4)]^-$, $[\text{PtCl}_3(\text{N}_2)]^-$ and $[\text{PtCl}_3(\text{CO})]^-$ all produce very similar isotope patterns (black), but the exact positions of the individual peaks are different (coloured traces). These data clearly depict the distinct differences in exact mass

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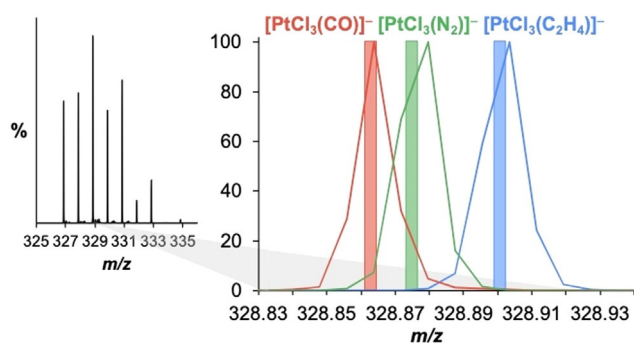


Figure 1. An overlaid spectrum of all three Pt complexes (left) shows the high resolution needed to distinguish these species. Individual peaks were identified (right) in experimental data for $[\text{PtCl}_3(\text{C}_2\text{H}_4)]^-$ (1, blue), $[\text{PtCl}_3(\text{N}_2)]^-$ (2, green), and $[\text{PtCl}_3(\text{CO})]^-$ (3, red).

for each of these complexes, and provide strong evidence of the authenticity of the N_2 complex 2. An overlaid plot of the full experimental isotope pattern and theoretical isotope pattern can be found in the Supporting Information (Figure S1).

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.^[49–52] 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 N_2 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

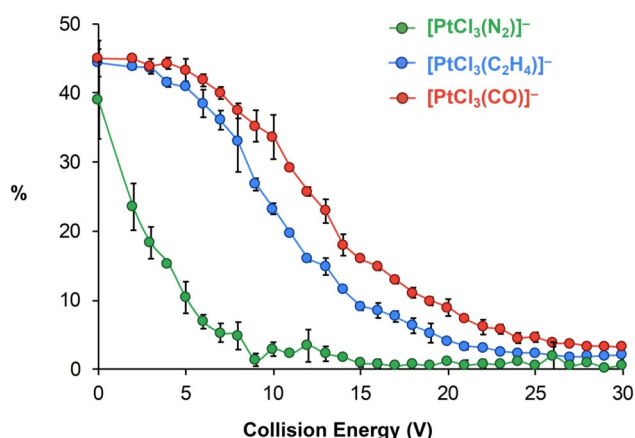


Figure 2. MS/MS data obtained for $[\text{PtCl}_3(\text{C}_2\text{H}_4)]^-$ (blue), $[\text{PtCl}_3(\text{N}_2)]^-$ (green) and $[\text{PtCl}_3(\text{CO})]^-$ (red) showing loss of $[\text{PtCl}_3(\text{L})]^-$ as L is removed. Collision energy at 50% of initial relative abundance: $[\text{PtCl}_3(\text{N}_2)]^- = 2.7$ V, $[\text{PtCl}_3(\text{C}_2\text{H}_4)]^- = 10.3$ V, $[\text{PtCl}_3(\text{CO})]^- = 13.1$ V.

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 N_2 and CO, requiring a collision energy of 10.3 V to produce the same degree of dissociation.

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,^[53] drift gas polarizability,^[54,55] shape,^[56] and charge state.^[57] Additionally, ions with a more delocalized charge are less prone to forming short-lived heterodimers with the drift gas molecules.^[46,58,59] 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.

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 $\text{CO} > \text{C}_2\text{H}_4 > \text{N}_2$. Because of the low number of atoms, calculations could be performed at a high level. Binding energies of N_2 , CO, and C_2H_4 to $[\text{PtCl}_3]^-$ 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).

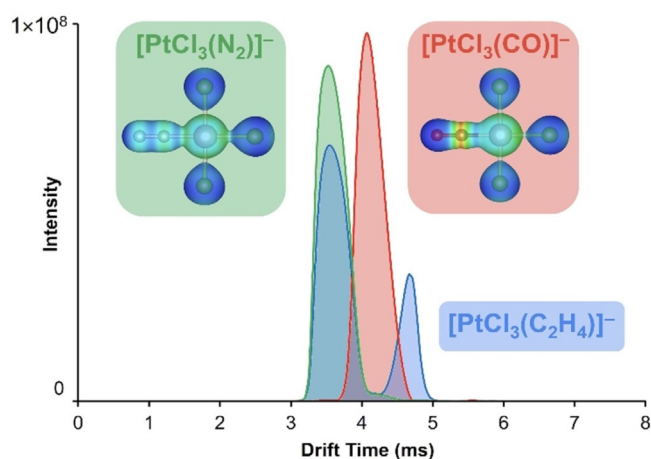


Figure 3. Ion-mobility spectrum for $[\text{PtCl}_3(\text{C}_2\text{H}_4)]^-$ (blue), $[\text{PtCl}_3(\text{N}_2)]^-$ (green) and $[\text{PtCl}_3(\text{CO})]^-$ (red); the area of each trace has been normalized to the same value. Structures of $[\text{PtCl}_3(\text{N}_2)]^-$ (left) and $[\text{PtCl}_3(\text{CO})]^-$ (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 ($0.1e \text{ \AA}^{-3}$).

The ligand dissociation energies for L ligands in complexes **1**, **2**, and **3** were compared to solvent molecules and O₂ for context (Figure 4 and the Supporting Information). N₂ 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 N₂. Dioxygen was the weakest binder of all, with less than half the binding strength of N₂ (unlike N₂, the strongest binding mode for O₂ was side-on rather than end-on).

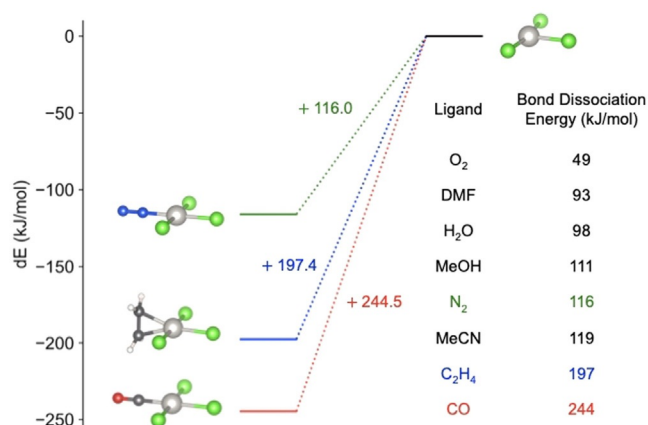


Figure 4. Ligand dissociation energies (LDE) calculated as reaction enthalpies for the dissociation reaction $\text{PtCl}_3\text{-L} \rightarrow \text{PtCl}_3 + \text{L}$. Comparison of C₂H₄, N₂ and CO (diagram) to that of common readily available compounds (see the table). See the Supporting Information for structures of all other ligands in the table.

Frontier molecular orbitals were examined for **1**, **2** and **3** (see the 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 N₂ bond length of 1.112 Å in **2** to established bond lengths in structurally 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 N₂ 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 co-workers 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 a feasible synthetic target. 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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Conflict of interest

The authors declare no conflict of interest.

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