



EU FT-ICR MS

# Open-shell Pt(III)-containing complexes characterized by IRMPD spectroscopy and quantum chemical calculations



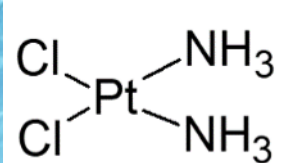
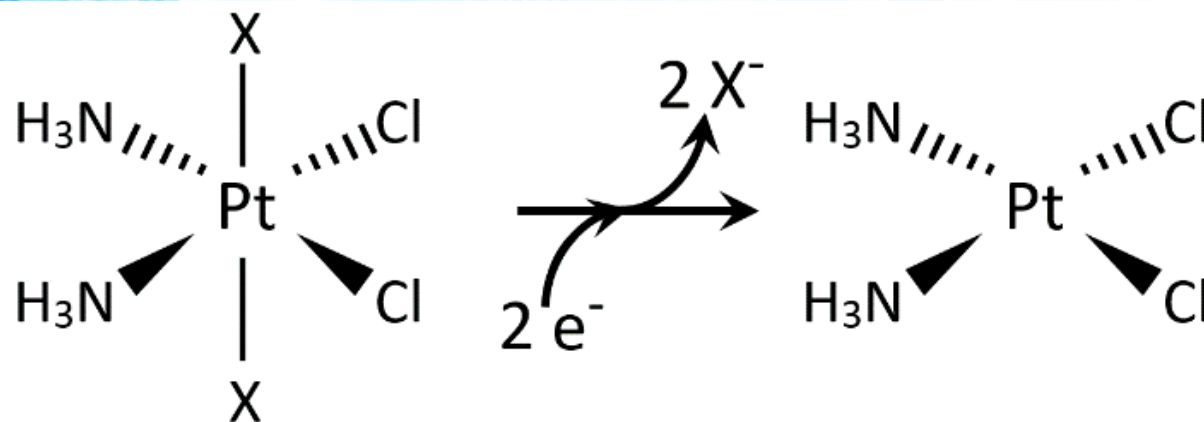
Davide Corinti

*Dipartimento di Chimica e Tecnologie del Farmaco,  
Sapienza- Università di Roma*

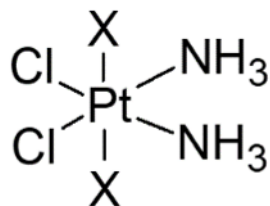


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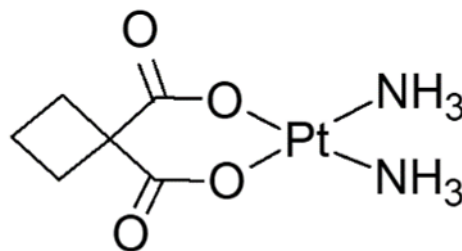
Prodrug activation,



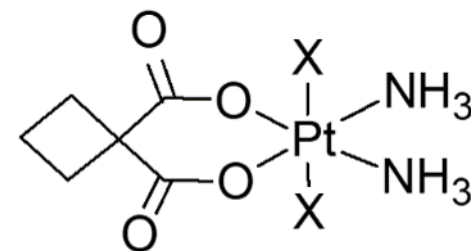
Cisplatin



**1** X=OH



Carboplatin



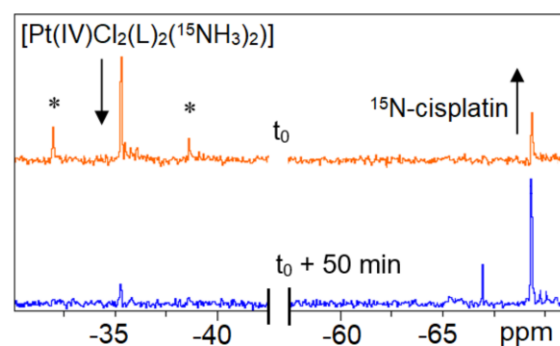
**2** X=OH

**3** X=CH<sub>3</sub>COO



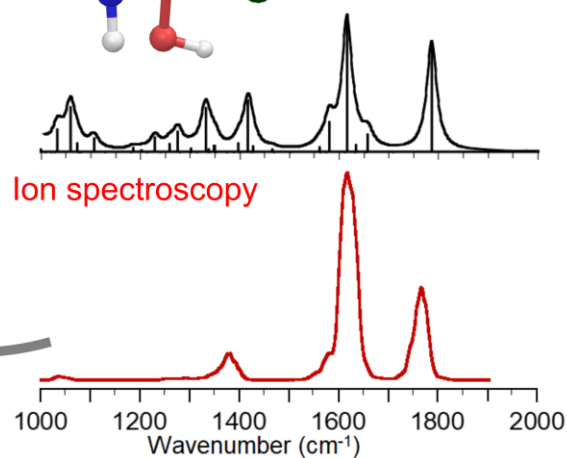
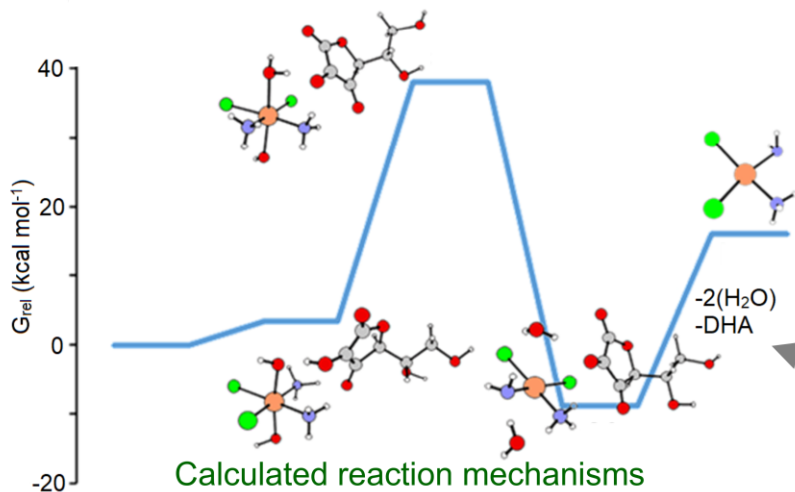
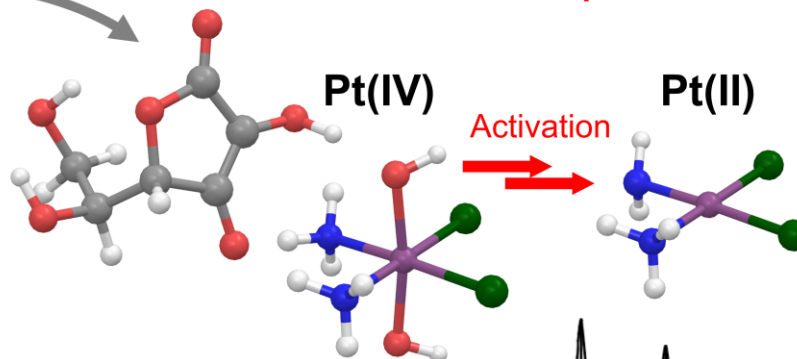


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Pt(IV) reduction in presence of ascorbic acid

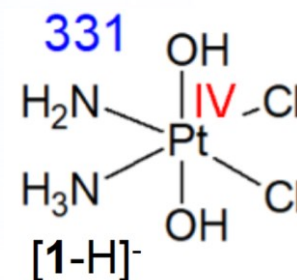
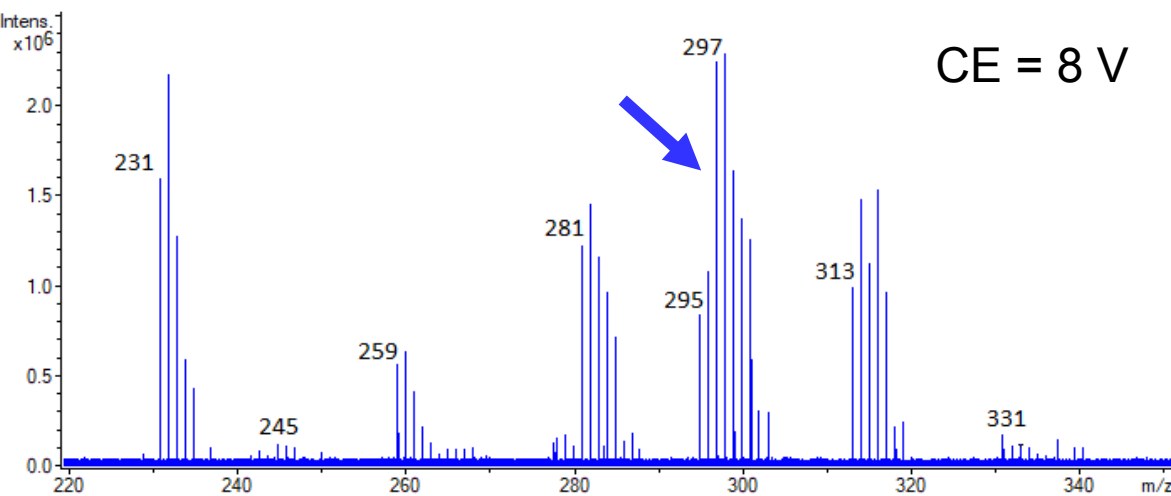
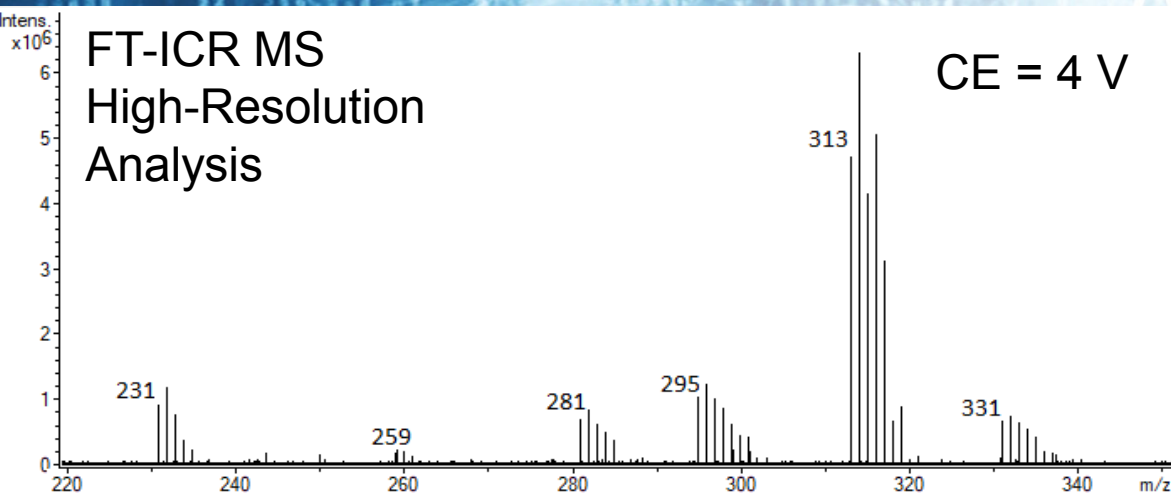
Characterization of bare reactive encounter complex



# CID mass spectrum of [1-H]<sup>-</sup> (*m/z* 331-337)



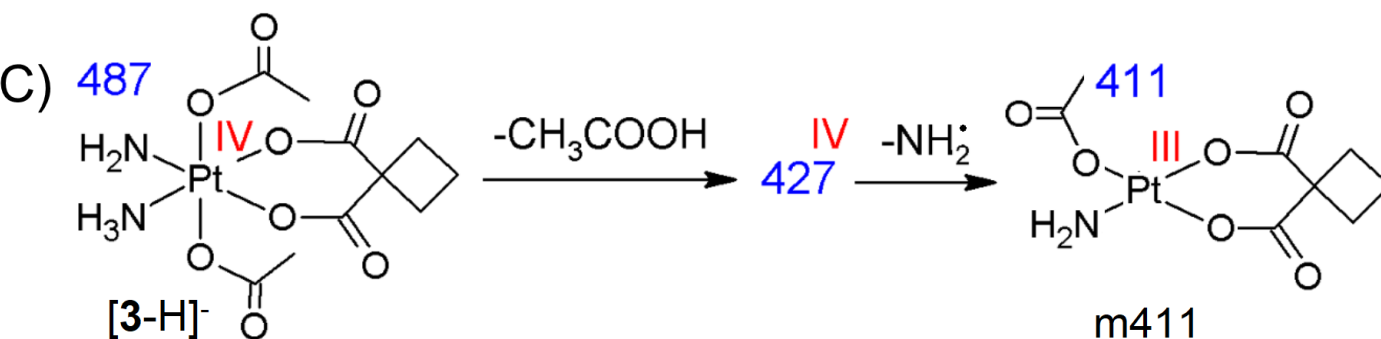
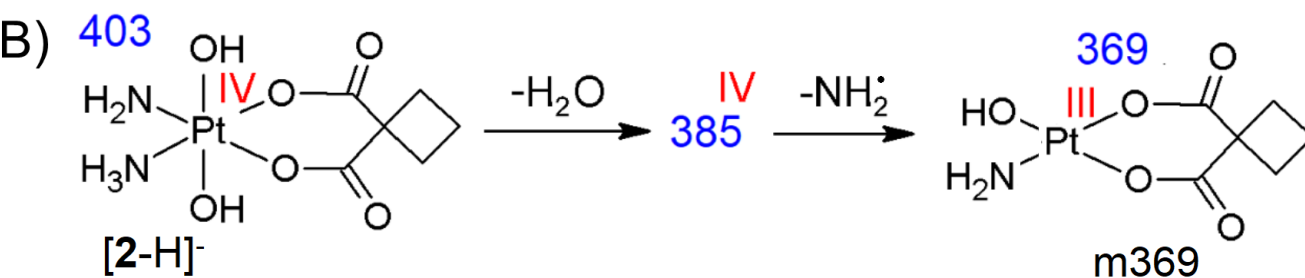
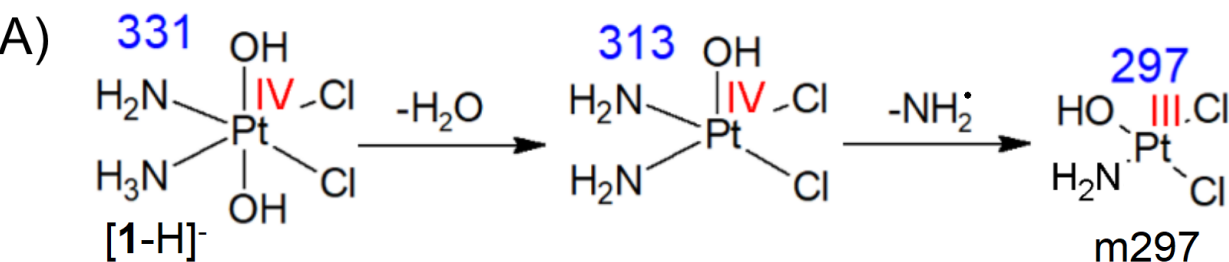
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D. Corinti et al., J. Am. Soc. Mass Spectrom. 30 (2019) 1881–1894



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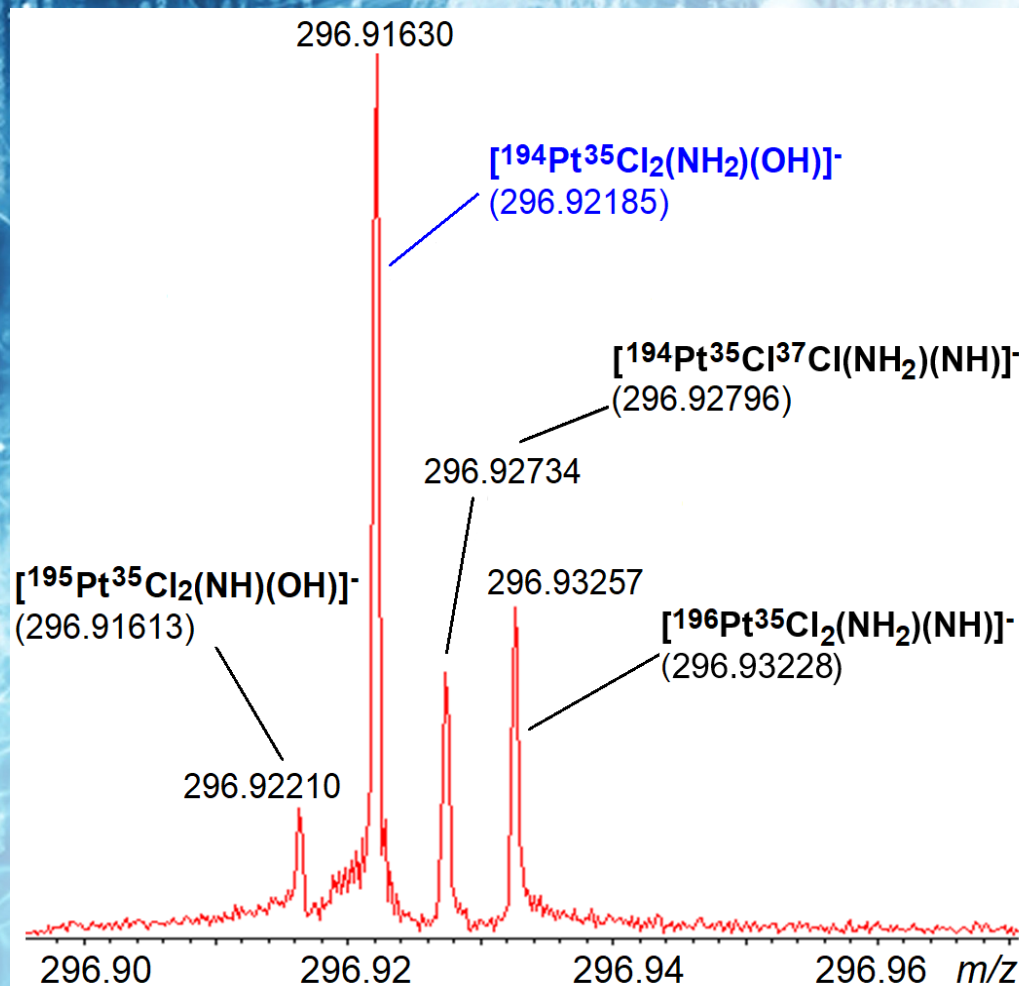
The  $m/z$  ratio of each species is indicated in **blue** and the formal oxidation state of platinum in **red**.

Each complex is negatively charged; charges are not made explicit





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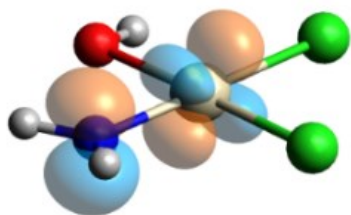
Excerpt of the CID mass spectrum of  $[1\text{-H}]^-$ . The assigned elemental composition is reported for each ion together with the corresponding calculated exact mass in Da (in brackets).

The ion corresponding to the Pt(III) containing complex is reported in **blue** while all other species are formal Pt(IV) complexes.

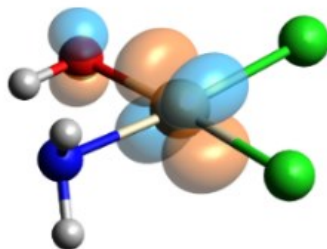


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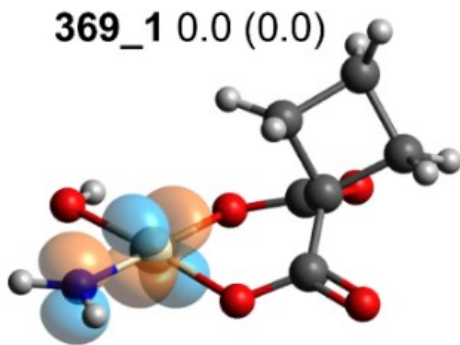
297\_1 0.0 (0.0)



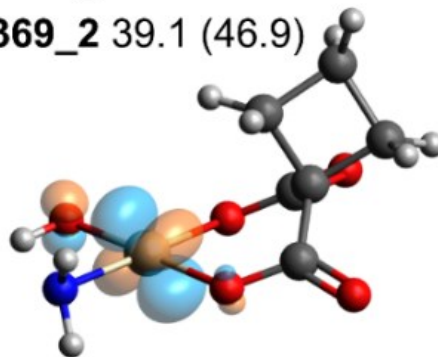
297\_2 40.2 (43.5)



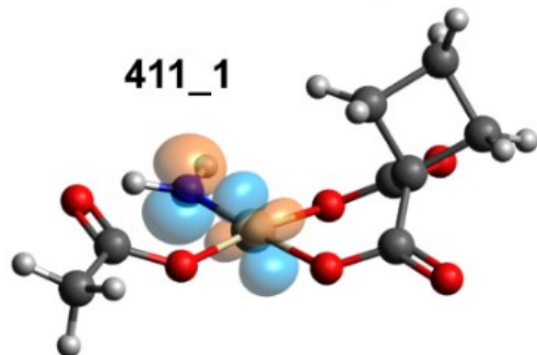
369\_1 0.0 (0.0)



369\_2 39.1 (46.9)



411\_1



Optimized geometries at the MP2/6-311++G(d,p) (Pt = def2-TZVP) level. SNOs obtained at the MP2/6-311++G(d,p) (Pt = def2-TZVP) level are shown with an isovalue of 0.20.

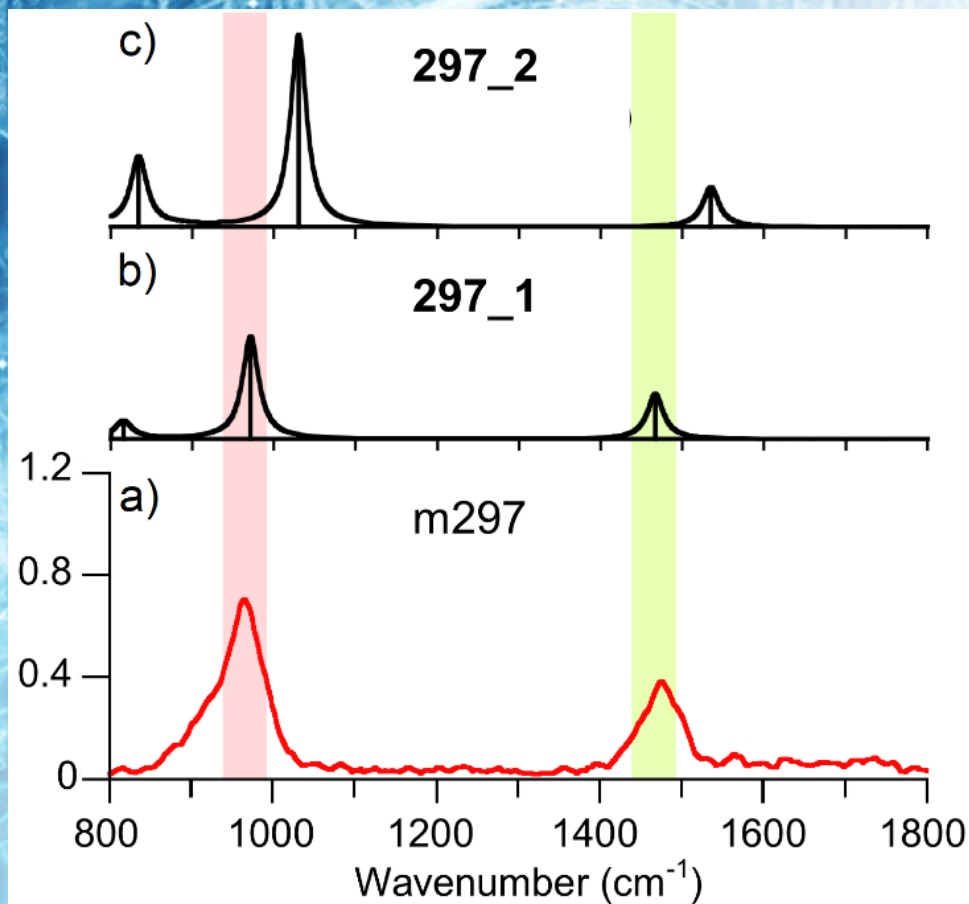
Relative free energies in  $\text{kJ mol}^{-1}$  are reported at the B3LYP and MP2 (in brackets) levels.



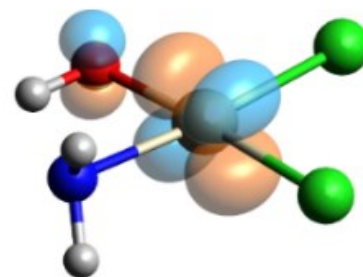


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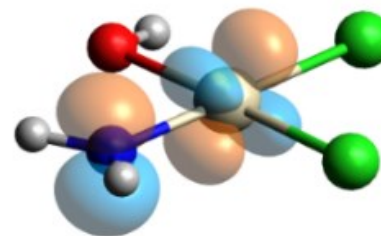
Experimental IRMPD spectrum of a) **m297** compared with the calculated IR spectra of b) **297\_1** and c) **297\_2** (scaling factor = 0.974).



297\_2 40.2 (43.5)



297\_1 0.0 (0.0)

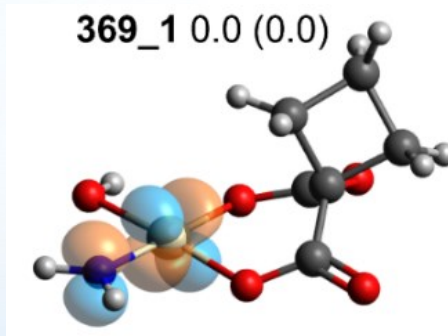
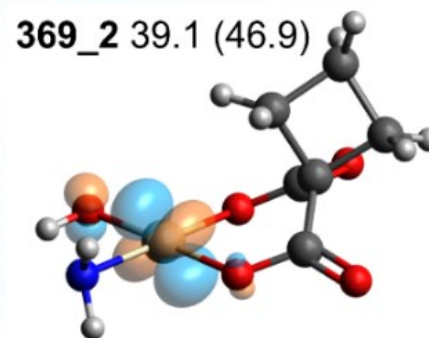
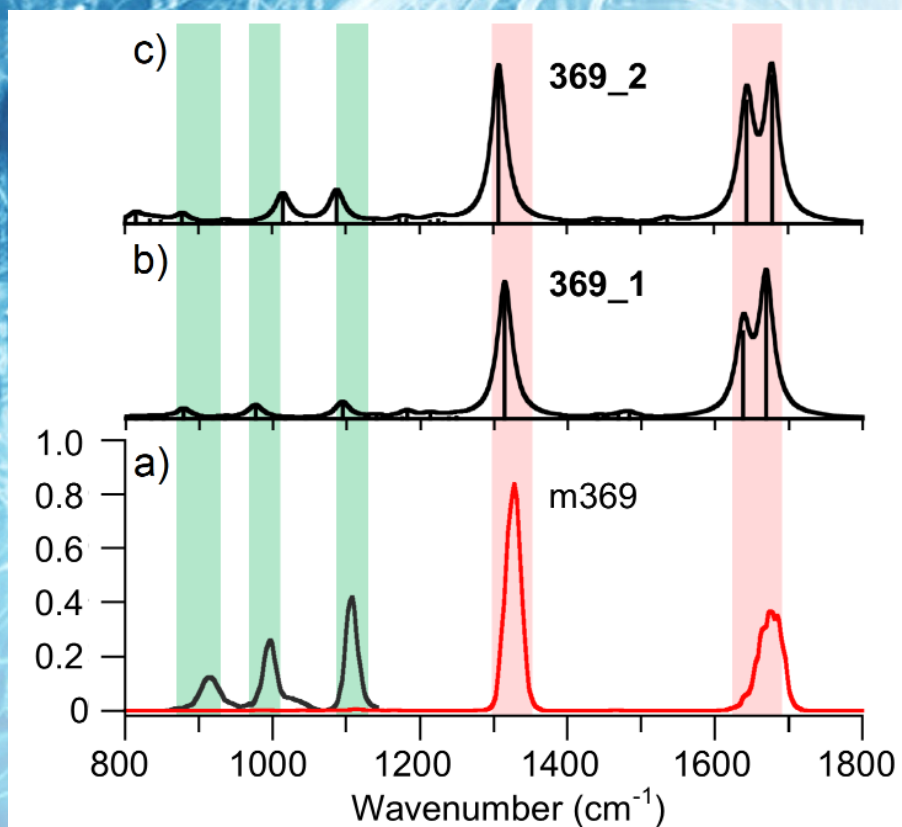






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Experimental IRMPD spectra of a) **m369** compared with the calculated IR spectra of b) **369\_1**, c) **369\_2** (scaling factor = 0.974).



# Conclusions



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- The gas-phase activation of  $[1-H]^-$ ,  $[2-H]^-$  and  $[3-H]^-$  has permitted to isolate and characterize platinum complexes with **formal metal oxidation state of +3**.
- The participation of platinum in the spin-density of the assayed ions with its  $d_{xz}$  orbital is a sign of the presence of a **radical character on platinum**.
- The **noninnocence of the amino ligand**, expressed in the high degree of delocalization of the unpaired electron onto the amino ligand can be identified as the main reason behind the unexpected finding of platinum(III)-containing ions



# Acknowledgement



**EU FT-ICR MS**



**Sapienza – Università di Roma**

Prof. Simonetta Fornarini  
Prof. Maria Elisa Crestoni  
Prof. Barbara Chiavarino



**Centre Laser  
Infrarouge d'Orsay**  
Prof. Debora Scuderi  
Prof. Philippe Maitre



**Università del Piemonte Orientale**

Prof. Domenico Osella  
Dr. Elisabetta Gabano



**Université Paris-Saclay**  
Dr. Gilles Frison



This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 731077.