Electronic Supplementary Material (ESI) for Dalton Transactions.

Square planar or octahedral after all? The indistinct solvation of platinum(II) –

Supplementary Material

Muhammad Saleh and Thomas S. Hofer[*]

Theoretical Chemistry Division
Institute of General, Inorganic and Theoretical Chemistry
Center for Chemistry and Biomedicine
University of Innsbruck, Innrain 80-82, A-6020 Innsbruck, Austria
E-Mail: T.Hofer@uibk.ac.at
Tel.: +43-512-507-57111
Fax: +43-512-507-57199

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[*] Corresponding author

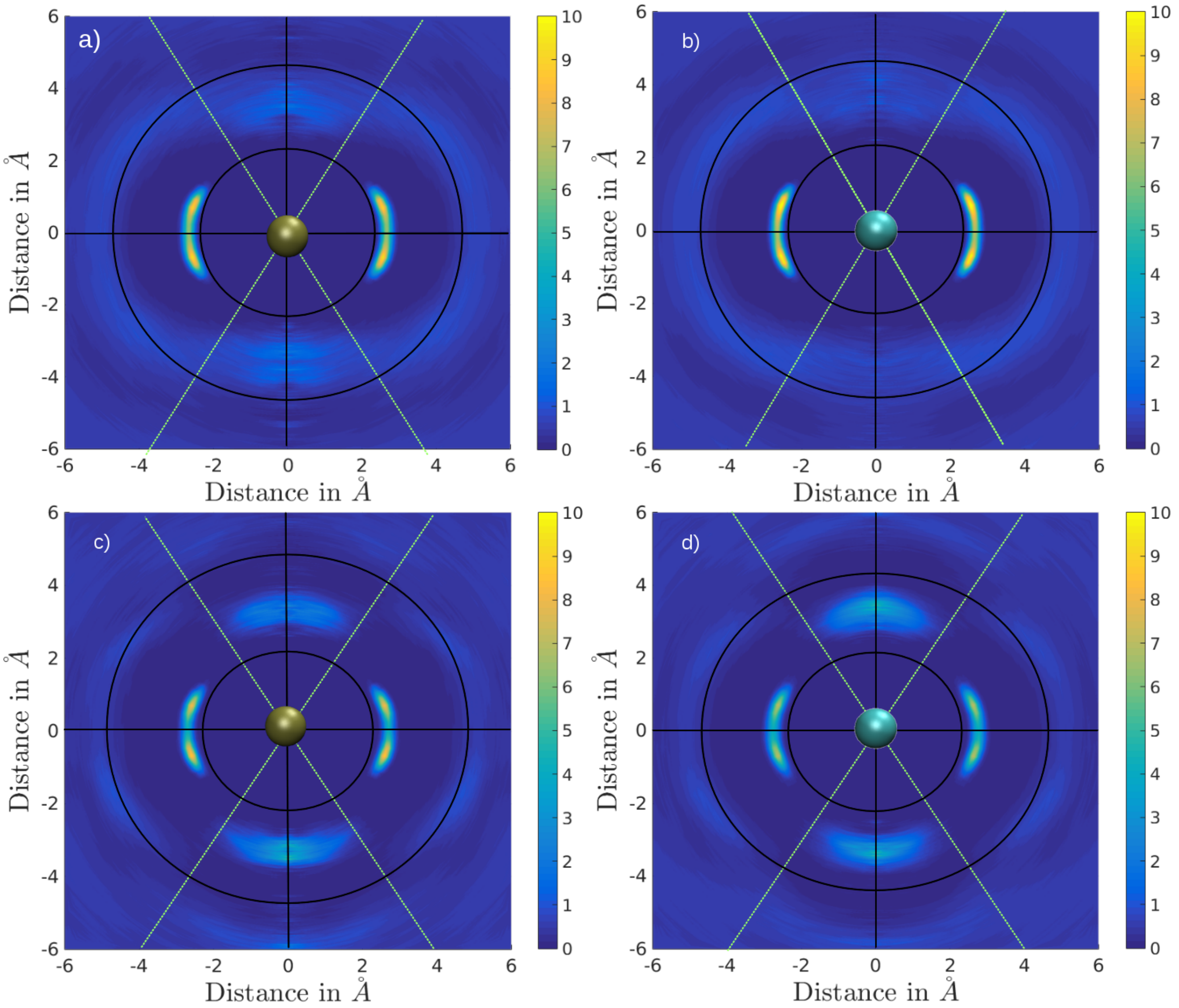

Figure S1: Angular-radial distribution (ARD) of a) Pd^{2+}-H[1] and b) Pt^{2+}-H (this work) in ammonia and c) Pd^{2+}-H[2] and d) Pt^{2+}-H[3] in aqueous solution obtained via the QMCF-MD simulation. The individual distributions lead to similar conclusions as drawn from the ion-L (L=N,O) ARDs depicted in figure 5 of the main article.

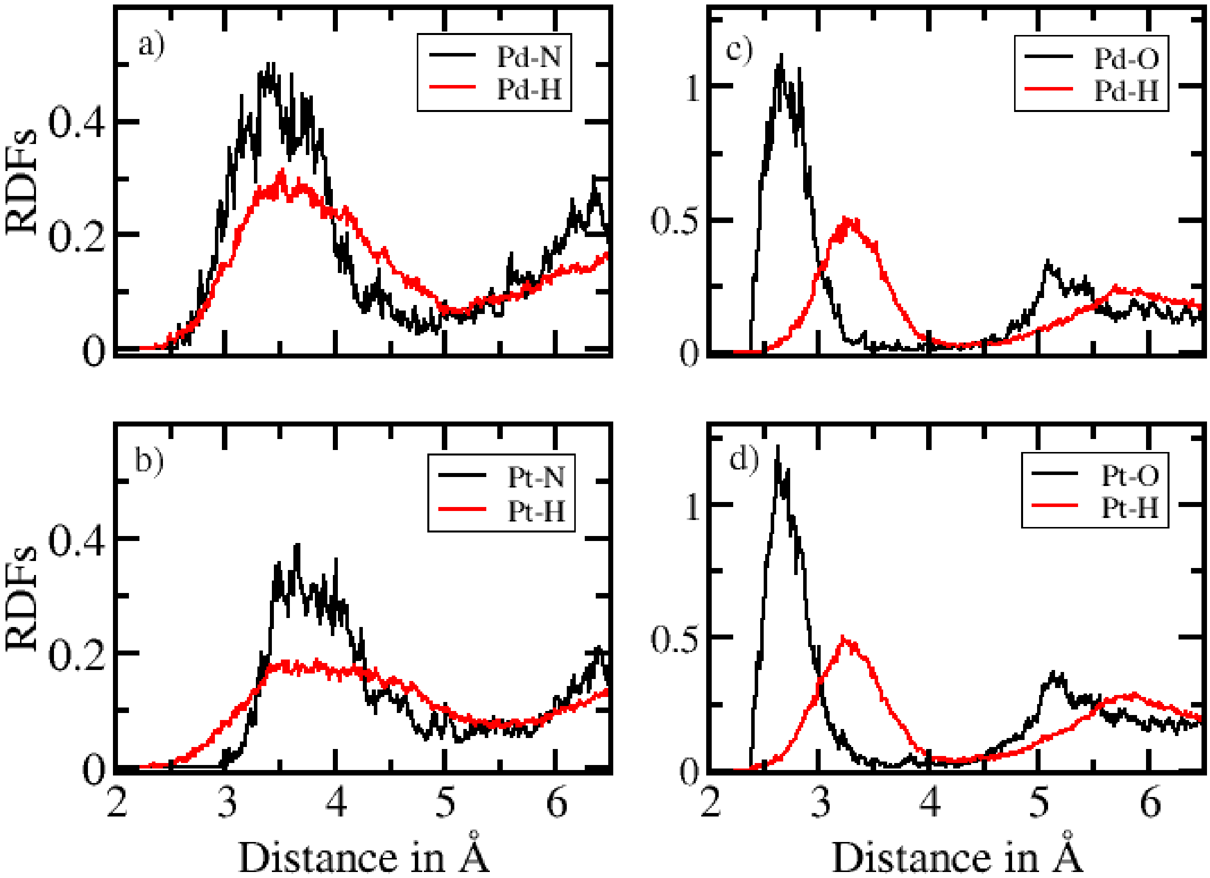

Figure S2: Pt-X (X = N,O; black) and Pt-H (red) radial distribution functions subject to a conical selection according to the definition depicted in the ARD plots (green-dashed lines in figure 5) obtained for liquid ammonia (left) and aqueous solution (right). While in the case of Pd(II) in ammonia the dipole orientation of the axial ligands is still visible, no preferential orientation can be observed in the Pt(II) case. These findings confirm the absence of an extended first hydration shell for Pt(II) in liquid ammonia, implying that this solute forms only a square-planar solvation shell. This is in contrast to the tetraherdally–elongated octahedral coordination observed in aqueous solution, in which for both solutes a strong dipole orientation is observed in the extended first hydration shell.

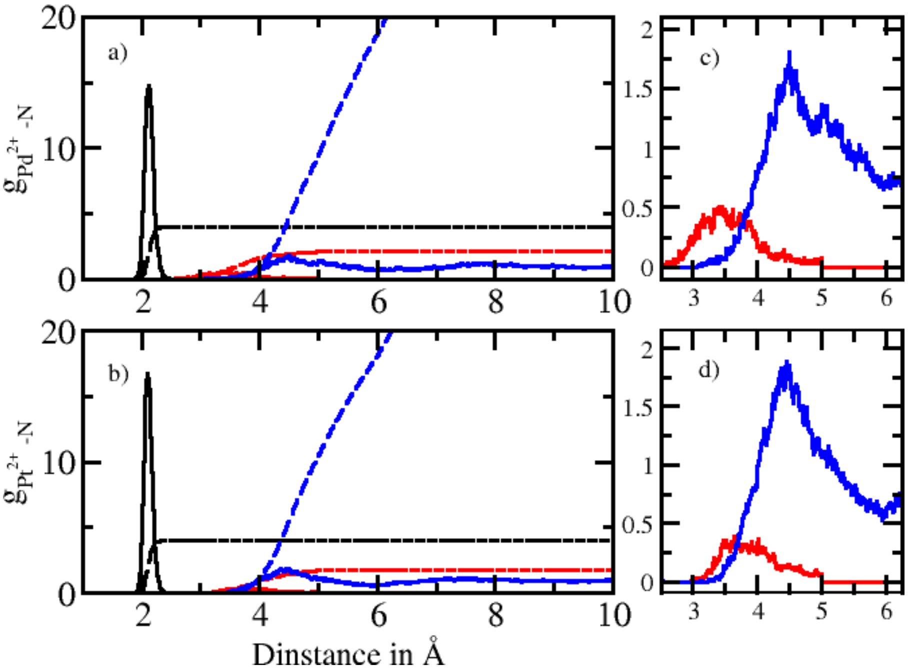

Figure S3: Decomposition of the radial distribution functions of a) Pd^{2+}-N and b) Pt^{2+}-N based on the conical selection. The black RDF represent the first shell, while red and blue depict the representation of the extended first and second shells, respectively. The respective running integration numbers are represented as dashed lines.

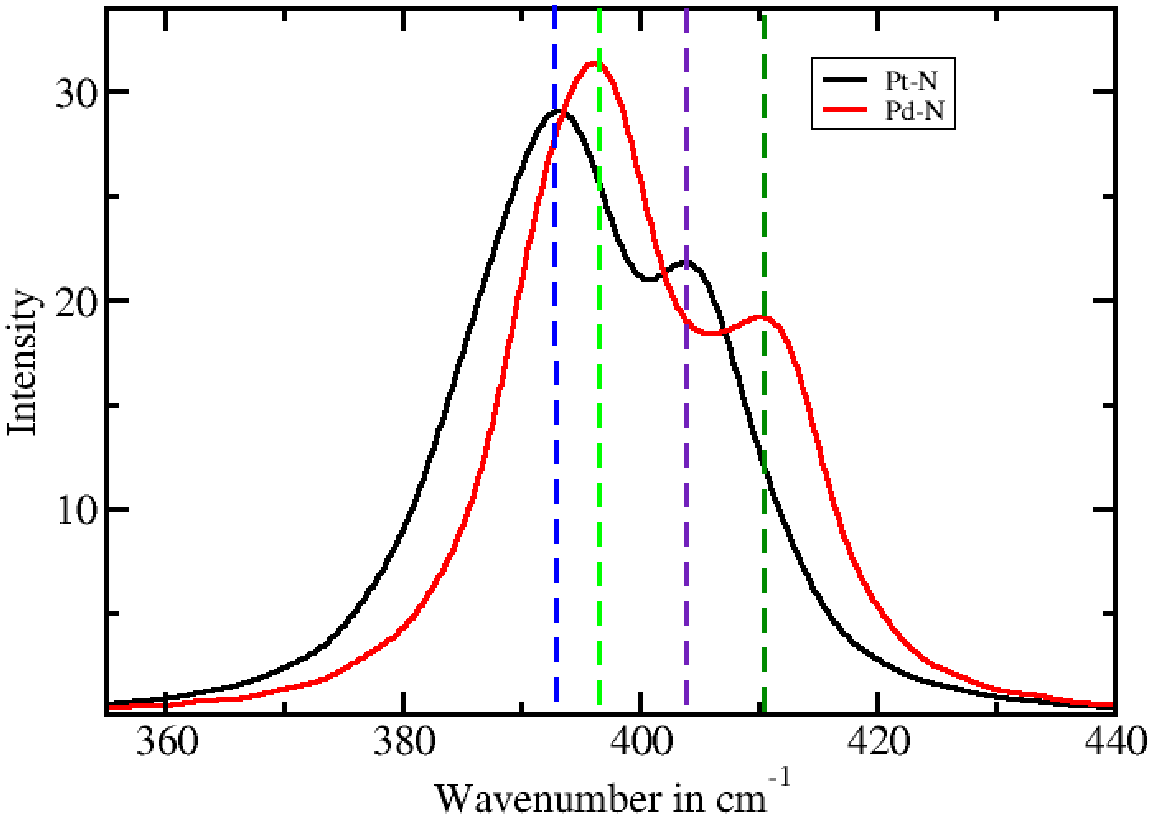

Figure S4: Power spectrum of ion-N vibration of Pt^{2+} (black) and Pd^{2+} (red) in liquid ammonia obtained via velocity autocorrelation function (VACF) and subsequent Fourier transform (FT). The dashed lines represents the wavenumbes of the respective peak maxima.

		QM/MM MD		EXAFS		
		r	CN	r	CN	ref
Pd-O	eq	2.07	4	2.006(4)	4	[2]
	ax	2.7	2	2.77(4)	2	
Pt-O	eq	2.017	4	2.017(5)	4	[3]
	ax	2.7	2	2.83(5)	2	

Table S1: Comparison of the ion-oxygen distance in Å of equatorial and axial water oxygen atoms in the first and extended first hydraton shell of aqueous Pd(II) and Pt(II) obtained via hybrid quantum mechanical/ molecular mechanical (QM/MM) molecular dynamics (MD) with results obtained from extended X-ray absorption fine structure (EXAFS) measurements. The small deviation results mainly from the fact that in case of the simulation the peak maximum of the associated ion-O RDF is give (*i.e* the distance of maximal occurrence), while the results of the EXAFS measurements correspond to the average distance. In case an RDF peak is subject to strong tailing as observed for the exteneded first shell,[2,3] the average value obtained via the EXAFS method is slightly larger compared to the value obtained via QMCF MD simulation.

Method	n	r	$\Delta E/n$
CCSD	1	2.012	-148.5
	2	2.100	-123.7
	4	2.107	-101.0
MP2	1	1.995	-165.1
	2	2.089	-132.7
	4	2.093	-108.3
HF	1	1.990	-150.3
	2	2.087	-122.6
	4	2.116	-95.3
BLYP	1	2.031	-202.5
	2	2.124	-154.0
	4	2.127	-119.6
B3LYP	1	2.002	-192.5
	2	2.096	-148.7
	4	2.105	-116.6
PBE	1	2.002	-205.4
	2	2.095	-157.3
	4	2.097	-123.9

Table S2: Average ion-N distance r in Å and the associated interaction energy ΔE per ligand n in kcal/mol obtained via energy minimisation of different $[\mathrm{Pt(NH_3)}_n]^{2+}$ clusters ($n = 1, 2, 4$) at different levels of theory. It can be seen that especially in the case $n = 4$ the Hartee-Fock level shows better agreement with the correlated ab initio methods CCSD than the different DFT methods and even MP2. Very similar results were obtained in a previous investigation of Pd(II) in liquid ammonia.[1]

Basis set	n	r	$\Delta E/n$
DZP	1	2.012	-148.5
	2	2.100	-123.7
	4	2.107	-101.0
cc-pVDZ	1	2.011	-150.9
	2	2.100	-126.1
	4	2.106	-103.2
cc-pVTZ	1	1.966	-150.0
	2	2.047	-126.9
	4	2.050	-104.3

Table S3: Average ion-N distance r in Å and the associated interaction energy ΔE per ligand n in kcal/mol obtained via coupled clusters single and double (CCSD) energy minimisation of different $[\mathrm{Pt(NH_3)}_n]^{2+}$ clusters ($n = 1, 2, 4$) at different basis sets. It can be seen that the differences among those basis lead only to a slight change of the binding charateristics while at the same time the computational demand was dramatically increased .

References

[1] M. Saleh and T. S. Hofer, *Dalton Trans.*, 2017, **46**(29), 9630–9638.

[2] T. S. Hofer, B. R. Randolf, S. A. A. Shah, B. M. Rode, and I. Persson, *Chem. Phys. Lett.*, 2007, **445**(4), 193–197.

[3] T. S. Hofer, B. R. Randolf, B. M. Rode, and I. Persson, *Dalton Trans.*, 2009, (9), 1512–1515.