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Electronic Supplementary Information

The Prediction of Strong O-H/M Hydrogen Bonding between Water and Square-planar Ir and Rh Complexes

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S1. Calculations at CCSD(T)/CBS level

To find equilibrium d distances, we calculated the interaction energies of eleven model systems with a water molecule and neutral metal complexes ($[\text{Ir}(\text{acac})(\text{en})]$, $[\text{Ir}(\text{acac})(\text{H}_2\text{O})_2]$, $[\text{Ir}(\text{acac})(\text{CO})_2]$, $[\text{Rh}(\text{acac})(\text{en})]$, $[\text{Rh}(\text{acac})(\text{H}_2\text{O})_2]$, $[\text{Rh}(\text{acac})(\text{CO})_2]$, $[\text{Pt}(\text{acac})(\text{CN})(\text{CO})]$, and $[\text{Pd}(\text{acac})(\text{CO})(\text{CN})]$) or negatively charged complexes ($[\text{Ir}(\text{acac})(\text{OH})_2]^{2-}$, $[\text{Ir}(\text{acac})(\text{CN})_2]^{2-}$, and $[\text{Ir}(\text{acac})(\text{CN})(\text{CO})]^-$). All the calculations were done on these model systems for d distance from 1.9 to 3.3 Å (**Figure S1**), at MP2 level, using *aug-cc-pVDZ-pp* basis set for the metal atom and *aug-cc-pVDZ* basis set for the other atoms. For the obtained equilibrium d distances, the MP2 and CCSD(T) interaction energies at the basis set limit were estimated.

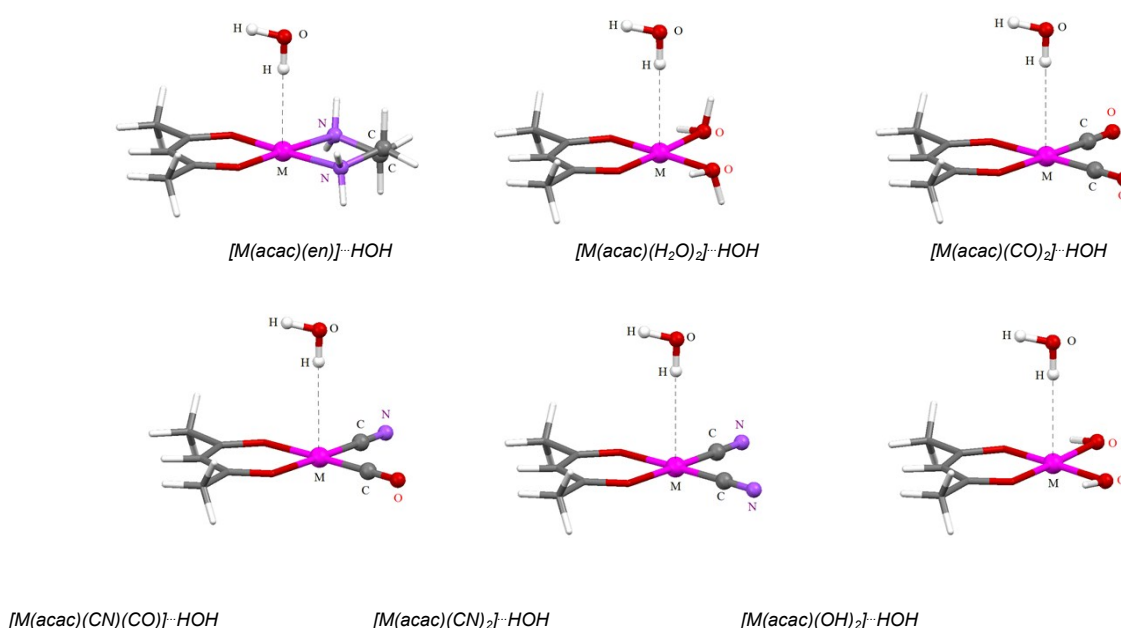


Figure S1. The model systems of water/metal-complexes, used to estimate the MP2 and CCSD(T) interaction energy at the basis set limit for O-H...M-L hydrogen bonds.

The interaction energies were calculated at the MP2 level using the Dunning's correlation consistent basis sets: cc-pVDZ/cc-pVDZ-pp, cc-pVTZ/cc-pVTZ-pp, cc-pVQZ/cc-pVQZ-pp, and aug-cc-pVDZ/aug-cc-pVDZ-pp (**Table S1 and S2**). In addition, we carried out the coupled cluster calculations with aug-cc-pVDZ/ aug-cc-pVDZ-pp basis sets. The MP2 interaction energy at the basis set limit (MP2 limit) was estimated by the method of Helgaker.^[S1] The CCSD(T) interaction

energy at the basis set limit (CCSD(T) limit) was estimated by the method of Sinnokrot and Sherrill.^[S2] The Δ term is the difference between the CCSD(T) and MP2 interaction energies using medium size basis set,^[S3] and in this case aug-cc-pVDZ basis set has been used (Table S1 and S2).

The results of calculations show that the strength of O-H/M-L interactions depends not only on the metal ion and ligand nature, but also on the metal ion and metal complex charge. For all the investigated systems, MP2/aug-cc-pVDZ & aug-cc-pVDZ-pp level gives results that are in excellent agreement with the very accurate CCSD(T) data for O-H/M-L interactions.

Table S1. Results of calculations on model systems with neutral Ir and Rh complexes, used to estimated the MP2 and CCSD(T) interaction energy at the basis set limit. The distance is expressed in Å and the energies in kcal/mol.

Level		Ir-en	Ir-(H ₂ O) ₂	Ir-(CO) ₂	Rh-en	Rh-(H ₂ O) ₂	Rh-(CO) ₂
MP2	cc-pVDZ cc-pVDZ-pp	-7.29	-5.57	-2.17	-6.69	-4.52	-1.94
MP2	cc-pVTZ cc-pVTZ-pp	-9.00	-6.49	-2.61	-8.10	-5.20	-2.26
MP2	cc-pVQZ cc-pVQZ-pp	-9.78	-6.85	-2.78	-8.75	-5.51	-2.41
MP2 limit		-10.75	-7.23	-2.98	-9.31	-5.79	-2.58
MP2	aug-cc-pVDZ aug-cc-pVDZ-pp	-9.33	-6.75	-2.81	-8.47	-5.48	-2.44
CCSD(T)	aug-cc-pVDZ aug-cc-pVDZ-pp	-8.41	-6.38	-2.66	-8.11	-5.40	-2.36
Δ		-0.92	-0.37	-0.15	-0.36	-0.08	-0.09
CCSD(T) limit		-9.83	-6.86	-2.83	-8.95	-5.71	-2.49
d		2.3	2.5	2.7	2.3	2.5	2.7

Abbreviations for model systems: Ir-en for [Ir(acac)(en)]·HOH, Ir-(H₂O)₂ for [Ir(acac)(H₂O)₂]·HOH, Ir-(CO)₂ for [Ir(acac)(CO)₂]·HOH, Rh-en for [Rh(acac)(en)]·HOH, Rh-(H₂O)₂ for [Rh(acac)(H₂O)₂]·HOH, and Rh-(CO)₂ for [Rh(acac)(CO)₂]·HOH model system.

Table S2. Results of calculations on model systems with neutral Pt and Pd complexes, used to estimated the MP2 and CCSD(T) interaction energy at the basis set limit. The distance is expressed in Å and the energies in kcal/mol.

Level		Ir-(OH) ₂	Ir-(CN) ₂	Ir-COCN	Pt-COCN	Pd-COCN
MP2	cc-pVDZ cc-pVDZ-pp	-10.47	-10.41	-5.44	-0.55	-0.29
MP2	cc-pVTZ cc-pVTZ-pp	-13.17	-11.69	-6.57	-1.01	-0.54
MP2	cc-pVQZ cc-pVQZ-pp	-14.54	-12.23	-7.05	-1.15	-0.61
MP2 limit		-15.49	-12.83	-7.57	-1.37	-0.72
MP2	aug-cc-pVDZ aug-cc-pVDZ-pp	-16.68	-12.06	-7.00	-1.11	-0.61
CCSD(T)	aug-cc-pVDZ aug-cc-pVDZ-pp	-18.54	-11.49	-6.65	-0.86	-0.51
Δ		1.86	-0.56	-0.35	-0.25	-0.10
CCSD(T) limit		-17.35	-12.26	-7.22	-1.12	-0.62
d		2.5	2.5	2.5	2.7	2.9

Abbreviations for model systems: Ir-(OH)₂ for [Ir(acac)(OH)₂]²⁻·HOH, Ir-(CN)₂ for [Ir(acac)(CN)₂]²⁻·HOH, Ir-COCN for [Ir(acac)(CN)(CO)]·HOH, Pt-COCN for [Pt(acac)(CN)(CO)]·HOH, and Pd-COCN for [Pd(acac)(CN)(CO)]·HOH model system.

The interaction was determined as the difference of the dimer energy and the sum of monomer energies. The basis set superposition error (BSSE) was properly eliminated in all cases using the counterpoise corrected method.^[S4] All the calculations were done on model systems for d distance (H···M distance) from 1.9 to 3.3 Å (Figure 1).

S2. Electrostatic potential maps of complexes

Gaussian09 program^[S5] was used for obtaining cube files for electrostatic potential and cube files for electron density for metal complexes, and the maps of electrostatic potential were made by using gOpenMol program.^[S6] We calculated the maps of electrostatic potential for all the investigated complexes in order to understand the difference in interaction energies for different complexes (Figures S2 and S3). Electrostatic potential ($V(r)$) was calculated at outer contour of electron density of 0.004 electrons/angstrom³.

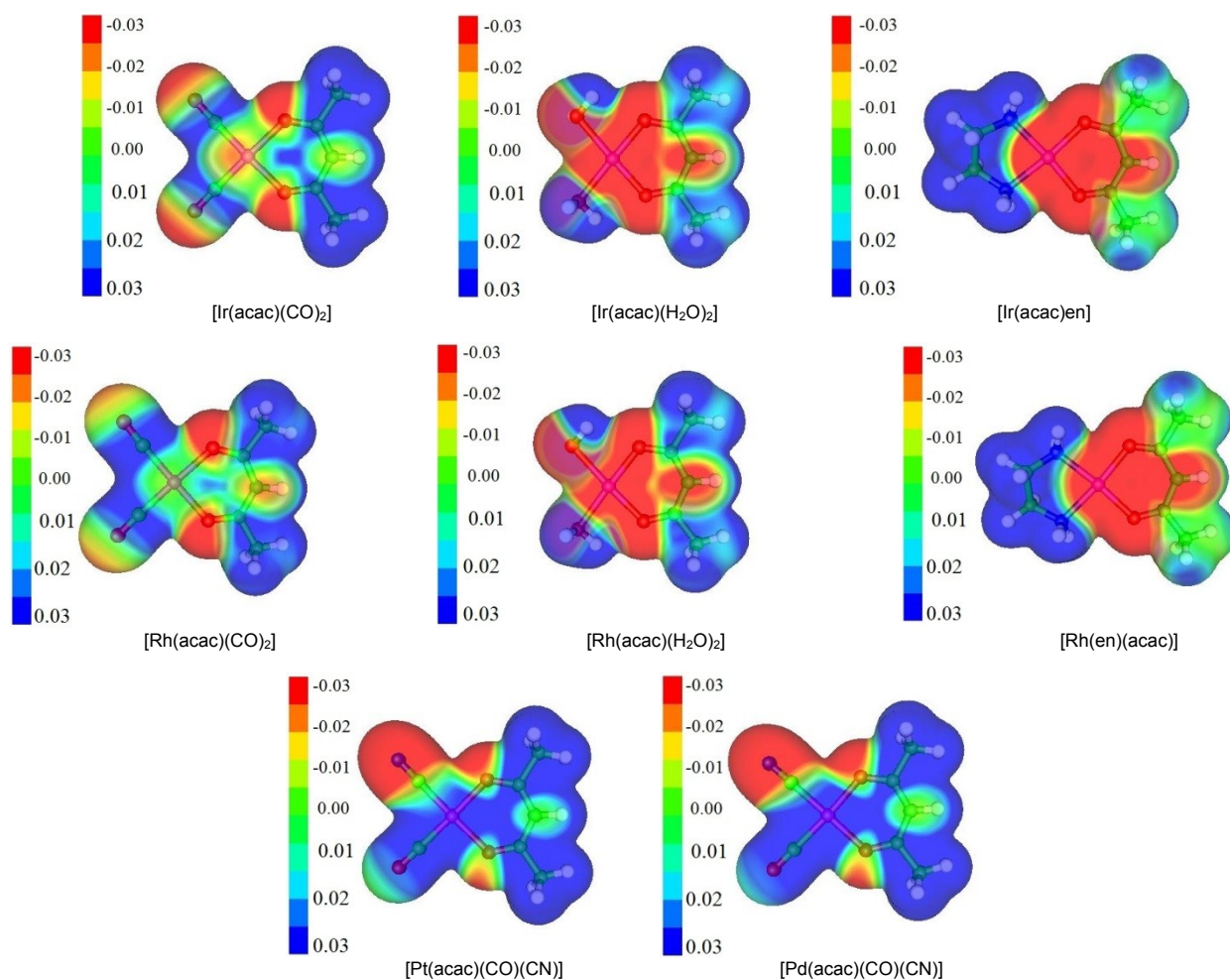


Figure S2. The maps of electrostatic potential for uncharged complexes.

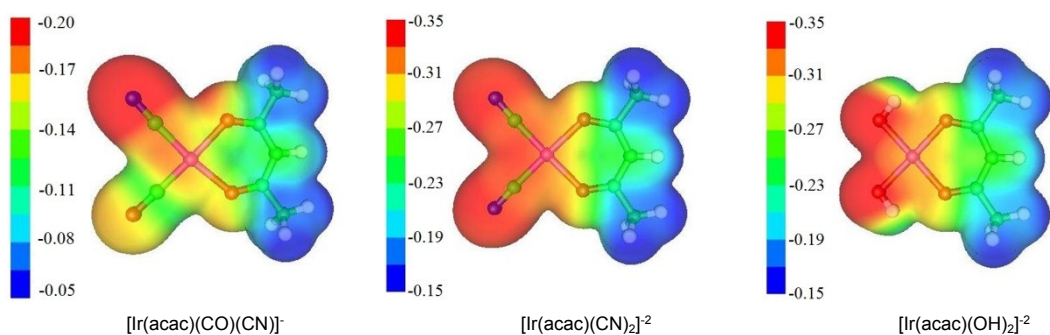


Figure S3. The maps of electrostatic potential for negatively charged complexes.

S3. Energy decomposition analysis

In order to understand better the nature of O-H/M interactions, it is also useful to analyse the interaction energy in terms of electrostatic, dispersion and exchange-repulsion components. The electrostatic interaction (ΔE_{ES}) between the distributed multipoles of isolated molecules was calculated using ORIENT program [S7]. The distributed multipoles were obtained from wave functions of the isolated monomers, using GDMA program [S8]. The wave functions were calculated on MP2 level using Gaussian09 program. The electron correlation energy (ΔE_{CORR}) was calculated as the difference between the CCSD(T) (ΔE_{TOT}) and Hartree–Fock interaction energy (ΔE_{HF}), and it is mainly attractive dispersion energy.

The interaction energies between metal complex and water molecule (ΔE) were determined as difference between the dimer energy ($E_{compl}/water$) and the sum of monomer energies ($E_{compl} + E_{water}$).

$$\Delta E = E_{compl}/water - (E_{compl} + E_{water})$$

The interaction energies were corrected for basis-set superposition error (BSSE) using the full counterpoise procedure [S4]. The corrected interaction energies were calculated at MP2 and HF level.

The difference between the Hartree–Fock interaction energy (ΔE_{HF}) and the electrostatic energy (ΔE_{ES}) can be considered as the exchange-repulsion energy (ΔE_{EX}). But the ΔE_{EX} component also includes other energy components, such as the polarization (ΔE_{POL}) and charge-transfer (ΔE_{CT}) components. **Table 1** lists the total and individual energy terms for O-H/M interactions.

Table S3. Energies and geometric data of O-H/M interactions. The distance is expressed in Å and the energies in kcal/mol.

Model system	d	ΔE_{TOT}	ΔE_{ES}	ΔE_{CORR}	ΔE_{EX}	Δq^*
Neutral complexes						
[Ir(acac)(en)]···HOH	2.30	-9.83	-8.62	-4.85	3.64	-32.40
[Ir(acac)(H ₂ O) ₂]···HOH	2.50	-6.86	-5.23	-2.44	0.81	-21.01
[Ir(acac)(CO) ₂]···HOH	2.70	-2.83	-0.15	-2.80	0.12	-0.53
[Rh(acac)(en)]···HOH	2.30	-8.95	-5.47	-4.50	1.02	-15.83
[Rh(acac)(H ₂ O) ₂]···HOH	2.50	-5.71	-2.99	-4.00	1.28	-15.33
[Rh(acac)(CO) ₂]···HOH	2.70	-2.49	0.02	-2.52	0.01	-2.17
[Pt(acac)(CN)(CO)]···HOH	2.70	-1.12	1.69	-3.26	0.45	2.71
[Pd(acac)(CN)(CO)]···HOH	2.90	-0.62	2.28	-2.37	-0.53	4.30
Charged complexes						
[Ir(acac)(CN)(CO)] ²⁻ ···HOH	2.50	-7.00	-3.16	-7.23	3.39	-9.01
[Ir(acac)(CN) ₂] ²⁻ ···HOH	2.50	-12.05	-8.06	-6.51	2.52	-19.99
[Ir(acac)(HO) ₂] ²⁻ ···HOH	2.50	-16.68	-13.68	-3.96	0.96	-60.01

* Δq = charge transfer

S4. Water/complex geometries and crystal structures

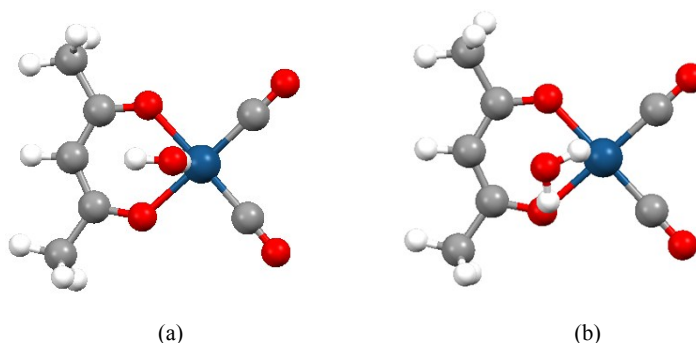


Figure S4. Model system [Ir(acac)(CO)₂]/H₂O before (a) and after (b) geometry optimization. Optimized structure is stabilized by 4.91 kcal/mol in comparison to the structure before optimization.

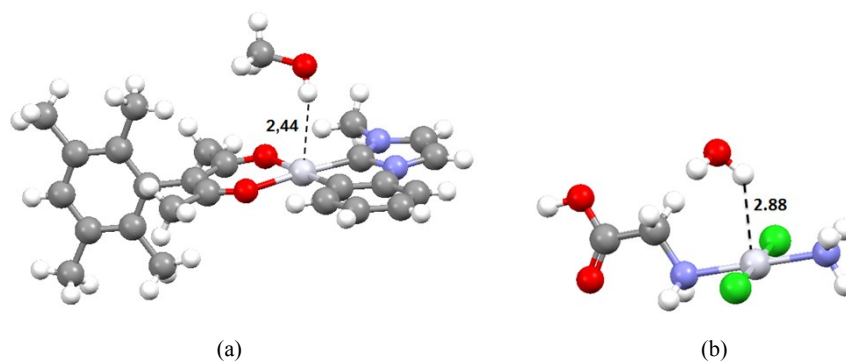


Figure S5. Crystal structures NOXJER ^[S9] (a) and CCAPGC11 ^[S10] (b) with O-H/Pt interaction.

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