COMPUTATIONAL CHEMISTRY DAY 2026

UNIVERSITY OF BELGRADE

FACULTY OF CHEMISTRY

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Are Energies of Hydrogen Bonds of Metal Complexes Predictable? Computational Study in the Gas Phase

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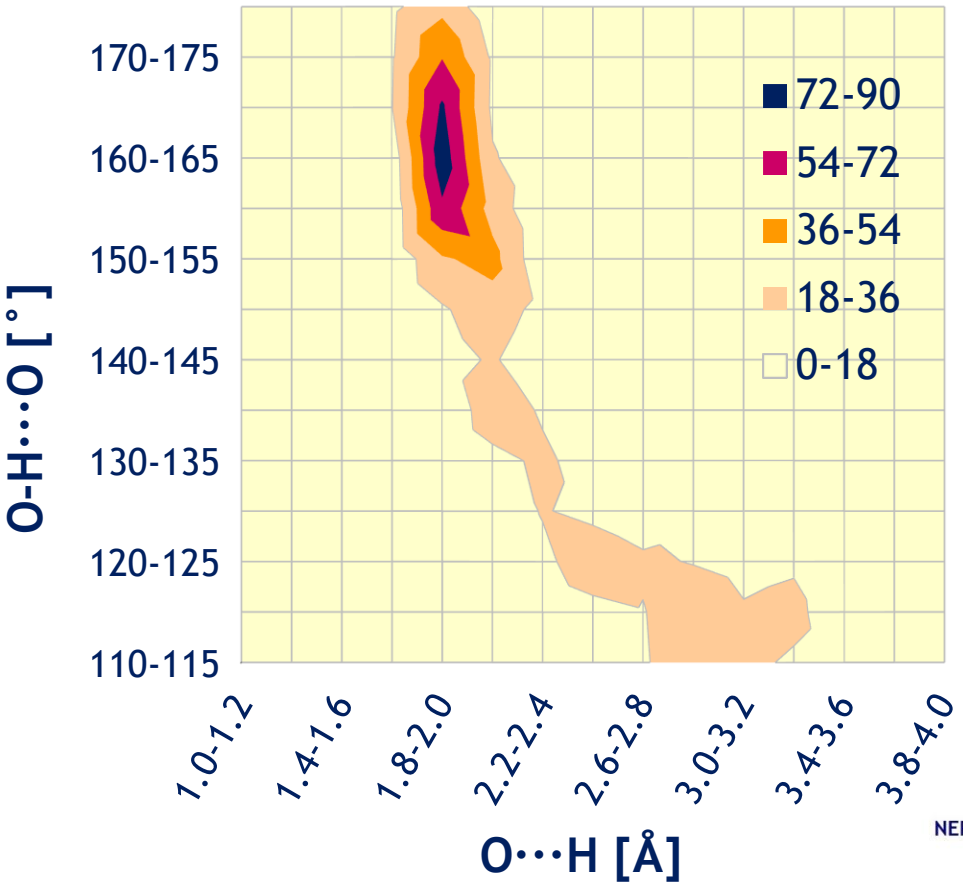
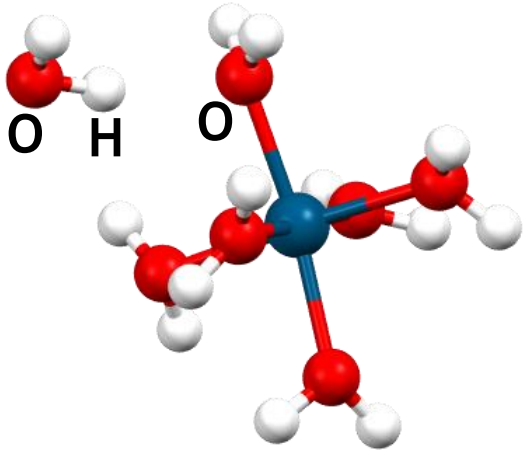
Zagreb, May 2026

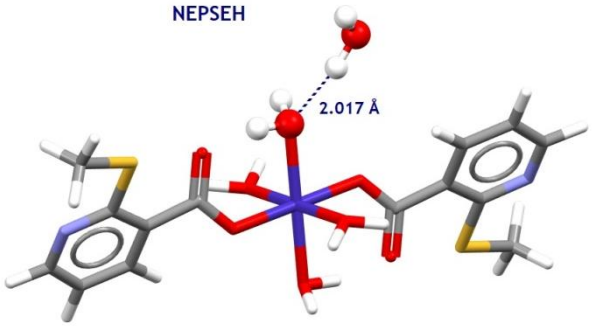
Aqua ligand as hydrogen bond acceptor

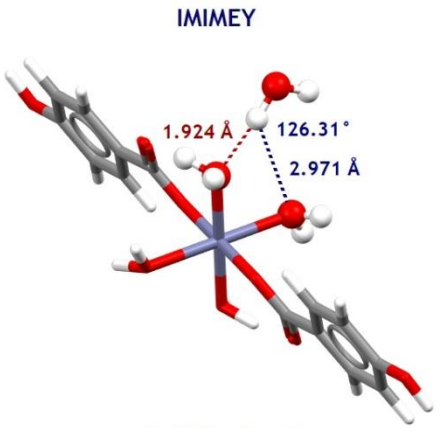


Cambridge Structural Database
CSD 5.43, November 2022



short (1.8 – 2.0 Å) and linear
long and non-linear



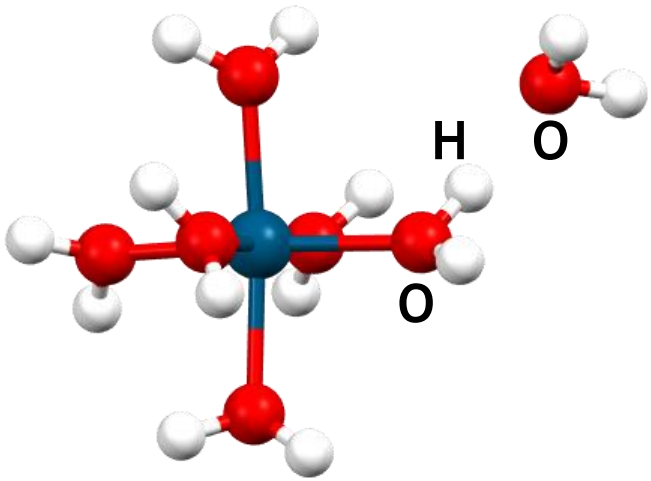


1229 hydrogen bonds

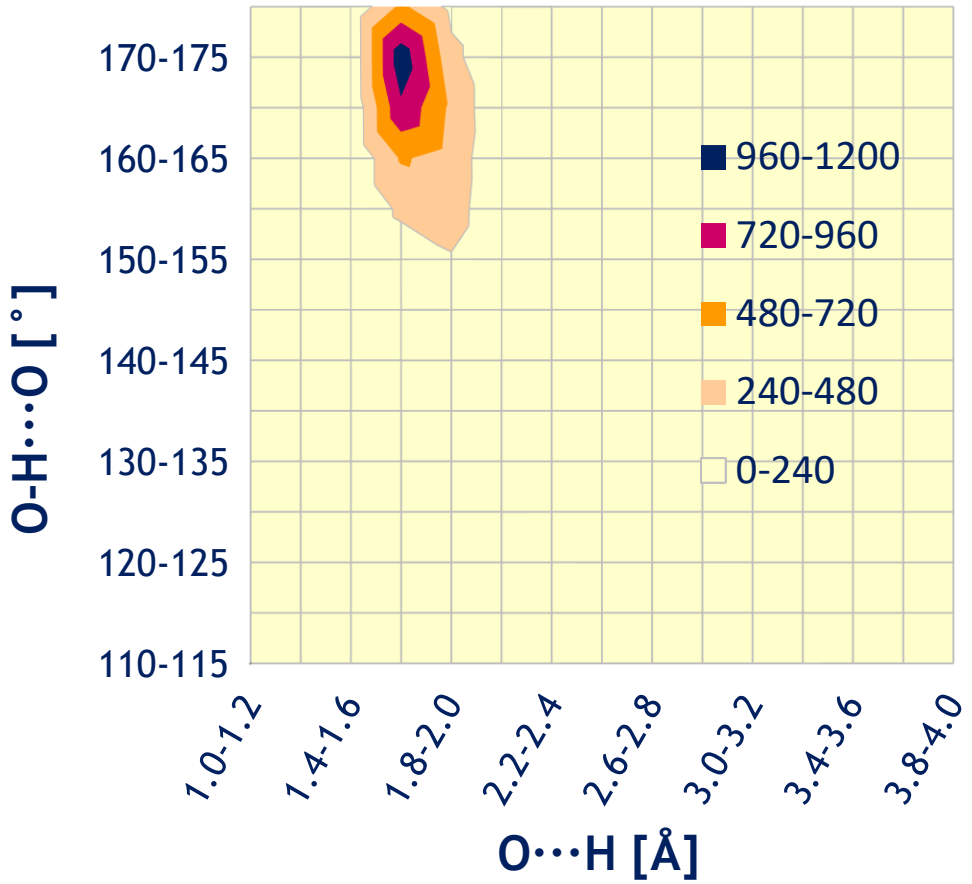
Malenov *et al.*, *Cryst. Growth Des.* **24** (2024) 8223-8233.

Aqua ligand as hydrogen bond donor

Cambridge Structural Database
CSD 5.43, November 2022



short (1.6 – 1.8 Å) and linear



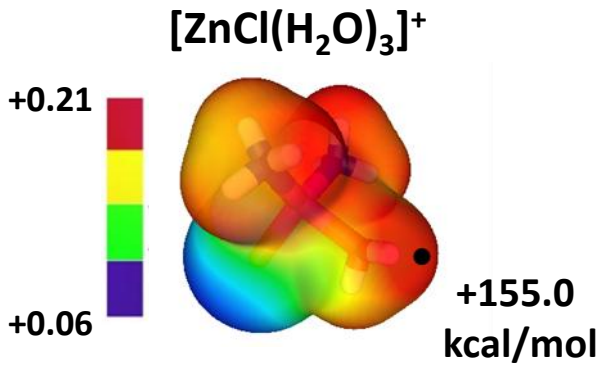
the most abundant type of hydrogen bonds of aqua ligands

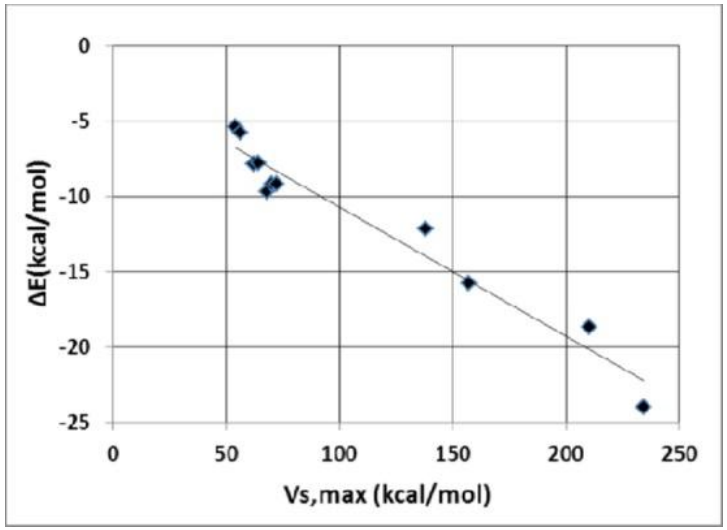
6579 hydrogen bonds

Andrić *et al.*, *Phys. Chem. Chem. Phys.* 2012, **14**, 10896.
Andrić *et al.*, *ChemPhysChem* 2016, **17**, 2035.

Aqua ligand as hydrogen bond donor

SYSTEM	INTERACTION ENERGY [kcal/mol]
$H_2O \cdots H_2O$	-4.4
neutral octahedral	
cis-$[ZnCl_2(H_2O)_4] \cdots H_2O$	-7.9
neutral tetrahedral	
$[ZnCl_2(H_2O)_2] \cdots H_2O$	-9.2
charged octahedral	
$[ZnCl(H_2O)_5]^+ \cdots H_2O$	-12.2
$[Zn(H_2O)_6]^{2+} \cdots H_2O$	-18.7
charged tetrahedral	
$[ZnCl(H_2O)_3]^+ \cdots H_2O$	-15.8
$[Zn(H_2O)_4]^{2+} \cdots H_2O$	-24.0





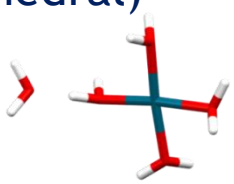
linear correlation between interaction energy and electrostatic potential (ESP)

Andrić *et al.*, *ChemPhysChem* 2016, **17**, 2035.

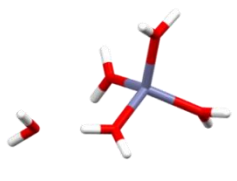
The Data Set

A set of **complexes** containing at least one **aqua or ammine ligand**, designed to study all **structural** and **electronic effects** on their hydrogen bonds:

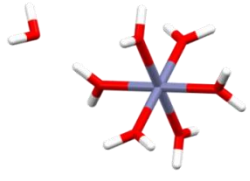
- geometry and coordination number (linear, square planar, tetrahedral, octahedral)
- metal oxidation state (M(I), M(II), M(III))
- different metals of the same transition row (Co(II), Ni(II), Zn(II))
- metals from different rows (Zn(II) and Cd(II), Pd(II) and Pt(II))
- other ligands (H_2O, NH_3, Cl^-)
- charge of the complex (0, +1, +2, +3)



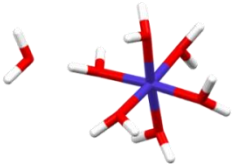
15
$[Pd(H_2O)_4]^{2+}\cdots H_2O$



37
$[Zn(H_2O)_4]^{2+}\cdots H_2O$

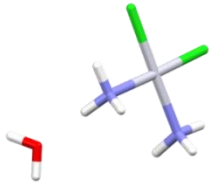


55
$[Zn(H_2O)_6]^{2+}\cdots H_2O$



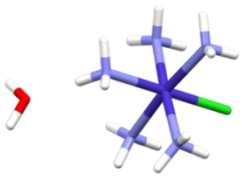
73
$[Co(H_2O)_6]^{3+}\cdots H_2O$

80
$[Ag(NH_3)_2]^{+}\cdots H_2O$



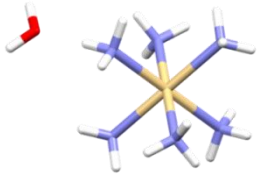
96
$[PtCl_2(NH_3)_2]\cdots H_2O$

76 aqua complexes
79 ammine complexes



119
$[CoCl(NH_3)_5]^{+}\cdots H_2O$

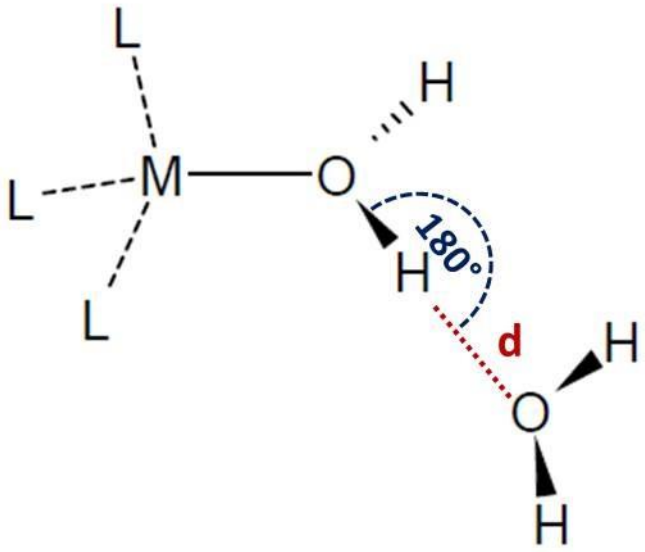
126
$[NiCl(NH_3)_4(H_2O)]^{+}\cdots H_2O$



142
$[Cd(NH_3)_6]^{2+}\cdots H_2O$

Malenov *et al.*, *Dalton Trans.* 2025, **54**, 12754.

Methodology



M06L-D3/def2-TZVPP

Gaussian 09 (D.01)

BSSE corrected interaction energies

*** in good agreement with CCSD(T)/CBS energies of hydrogen bonds**

SAPT2/def2-TZVP

PSI4 (1.7.0)

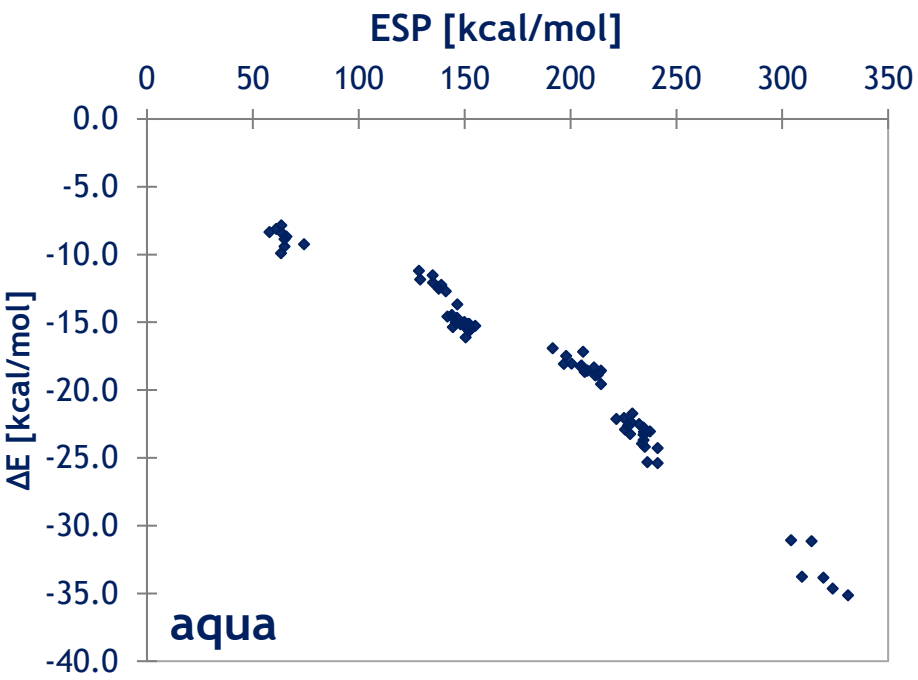
SAPT2 = ELST + EXCH + IND + DISP

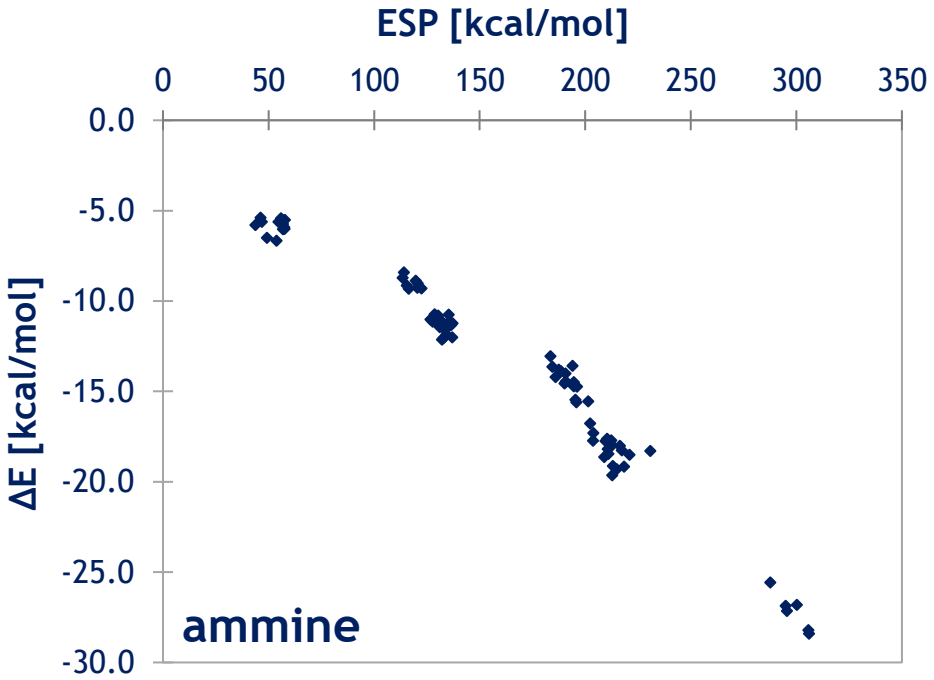
Electrostatic potentials on interacting hydrogen atoms

Gaussian 09 (D.01) and internal Python script

* Živković *et al.*, *Cryst. Growth Des.* 2022, **22**, 148.

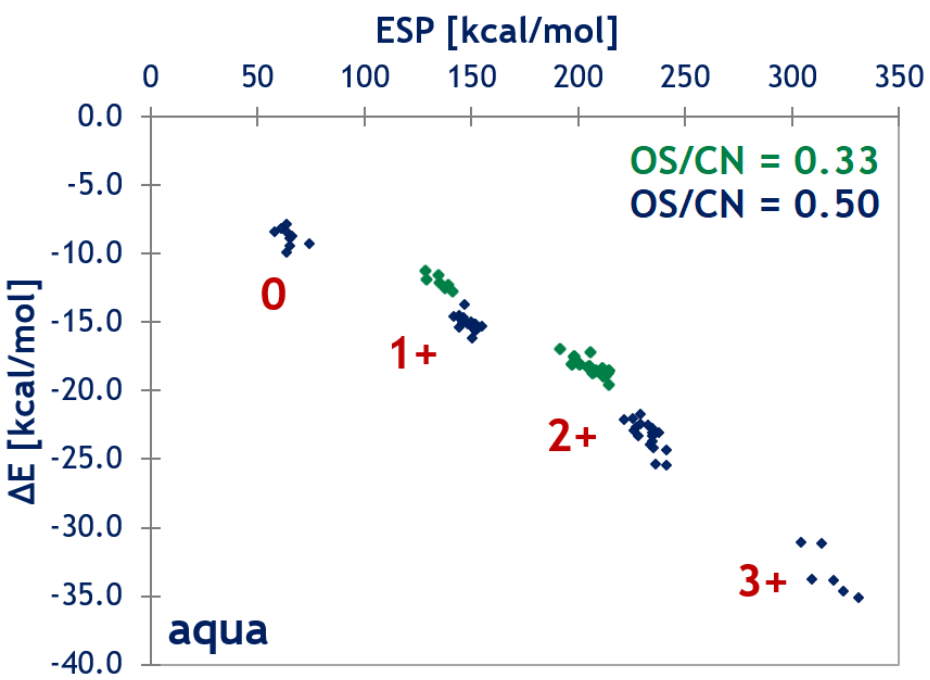
Interaction energy vs. hydrogen electrostatic potential

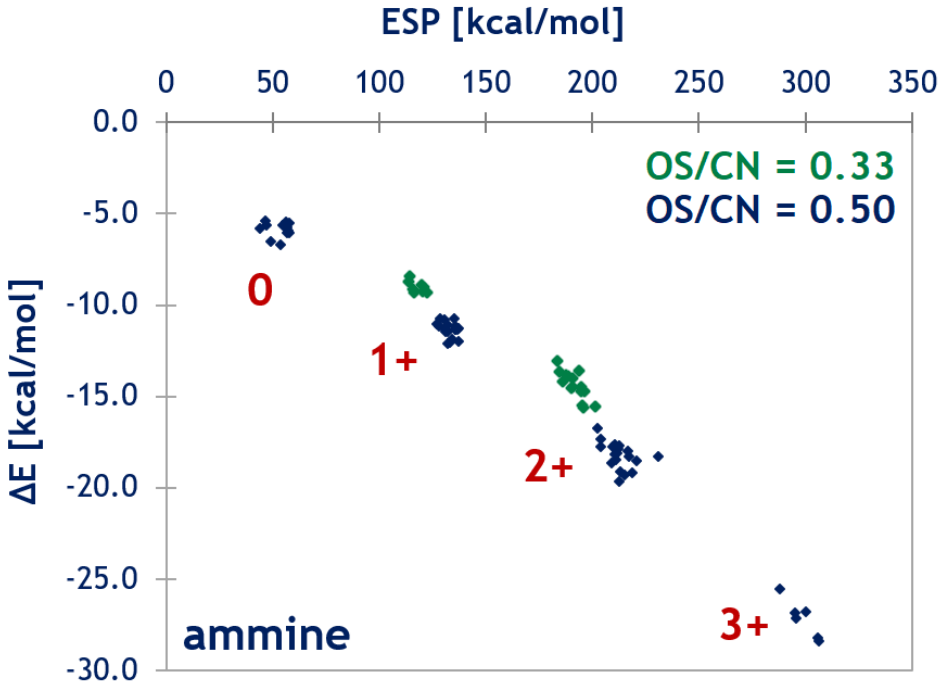




Malenov *et al.*, *Dalton Trans.* 2025, **54**, 12754.

Clustering of hydrogen bonds

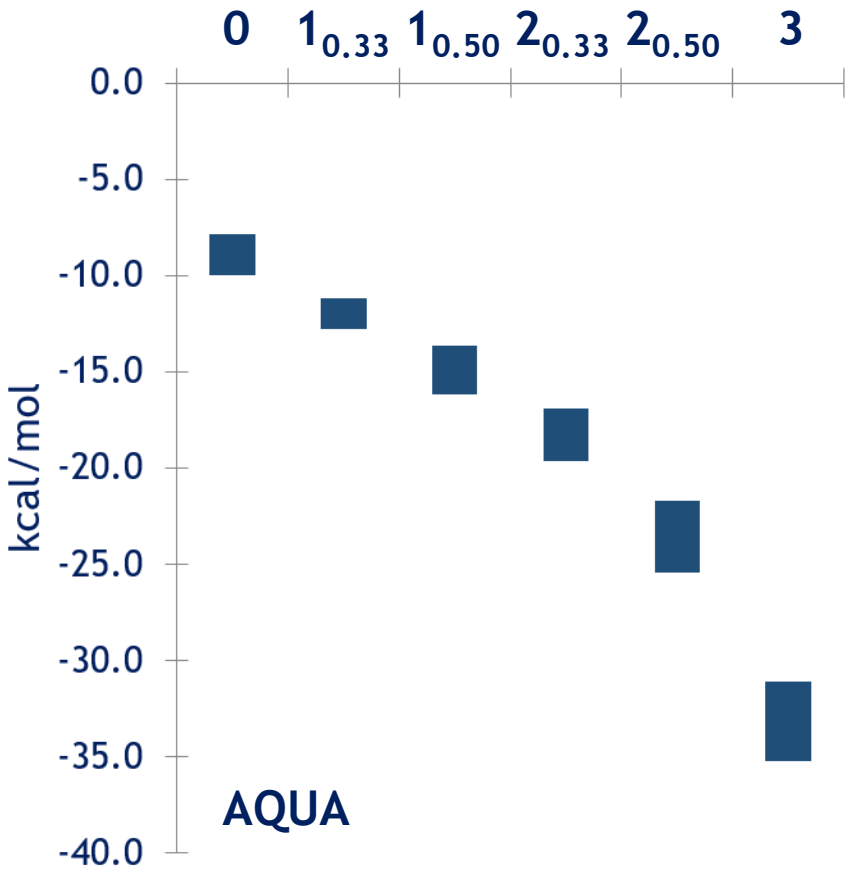


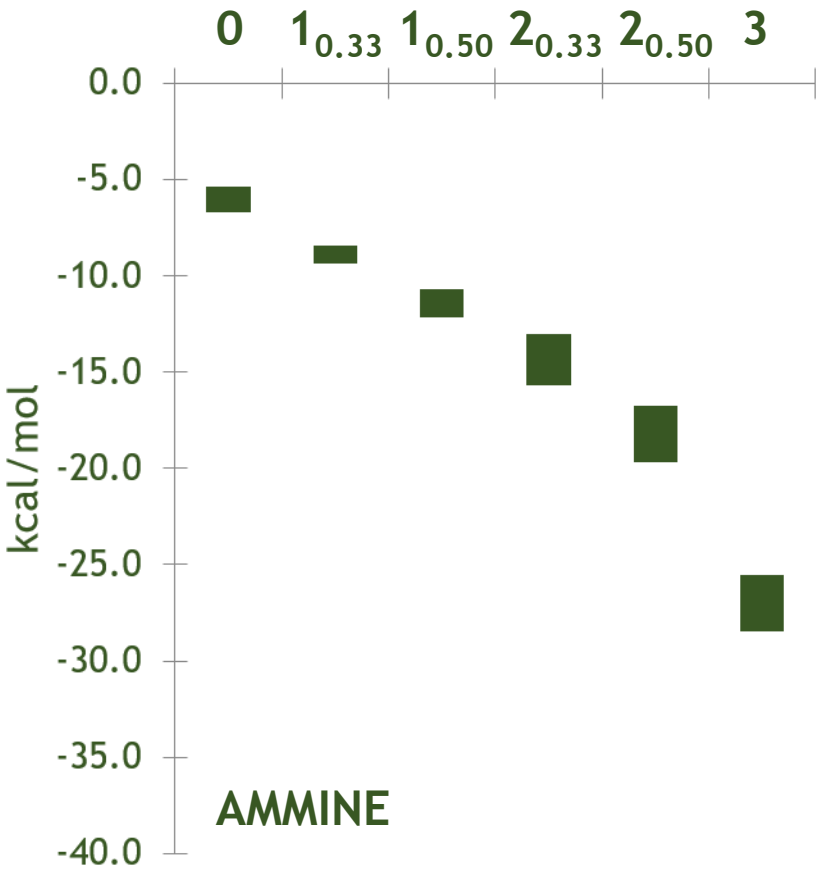


Malenov *et al.*, *Dalton Trans.* 2025, **54**, 12754.

Factors influencing hydrogen bond strength

- charge
- oxidation state/coordination number (OS/CN) ratio





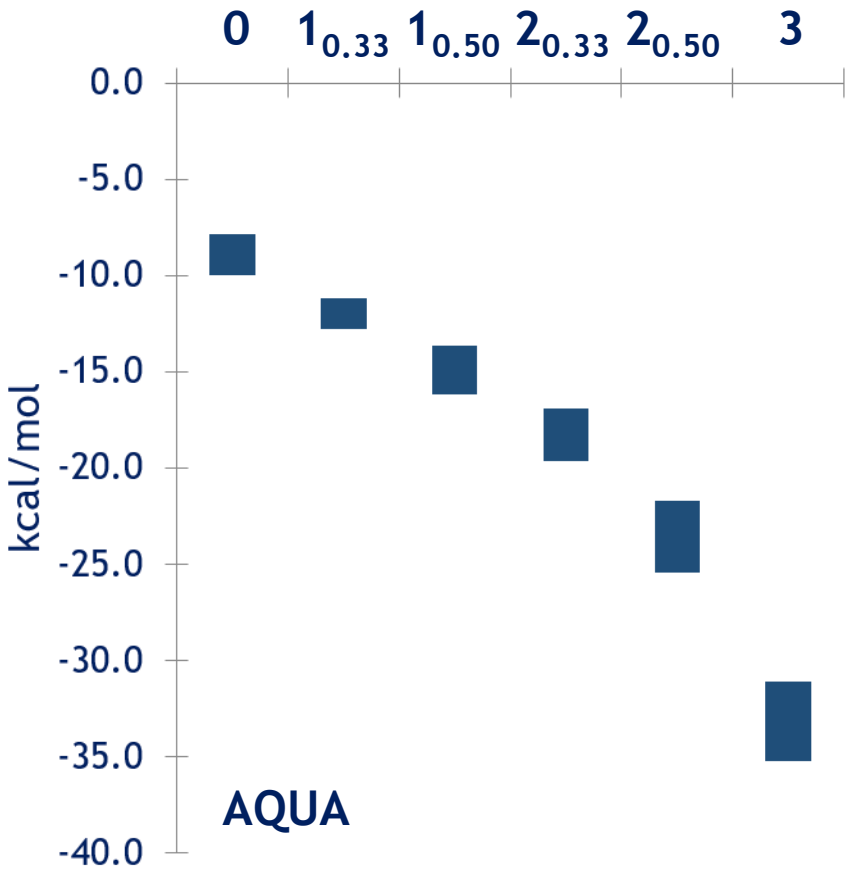
all other studied factors practically negligible

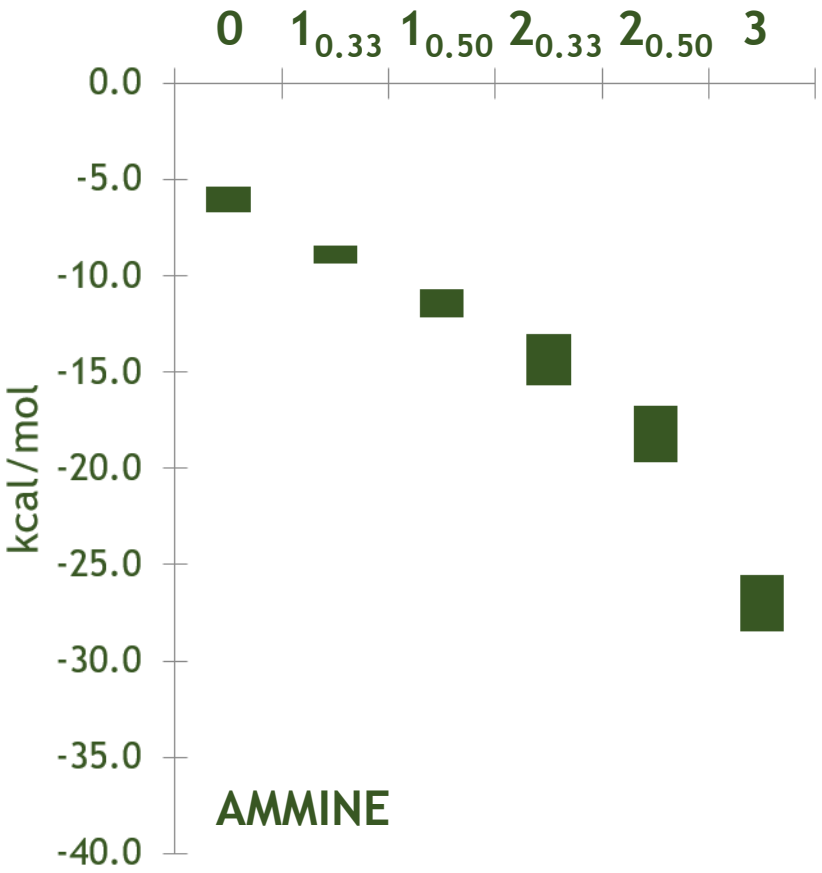
Malenov *et al.*, *Dalton Trans.* 2025, **54**, 12754.

Classification of complexes according to their hydrogen bonds

types of complexes - $CHARGE_{OS/CN}$ *labelling*

$2_{0.33}$ = *2+ charged complex with OS/CN ratio 0.33*



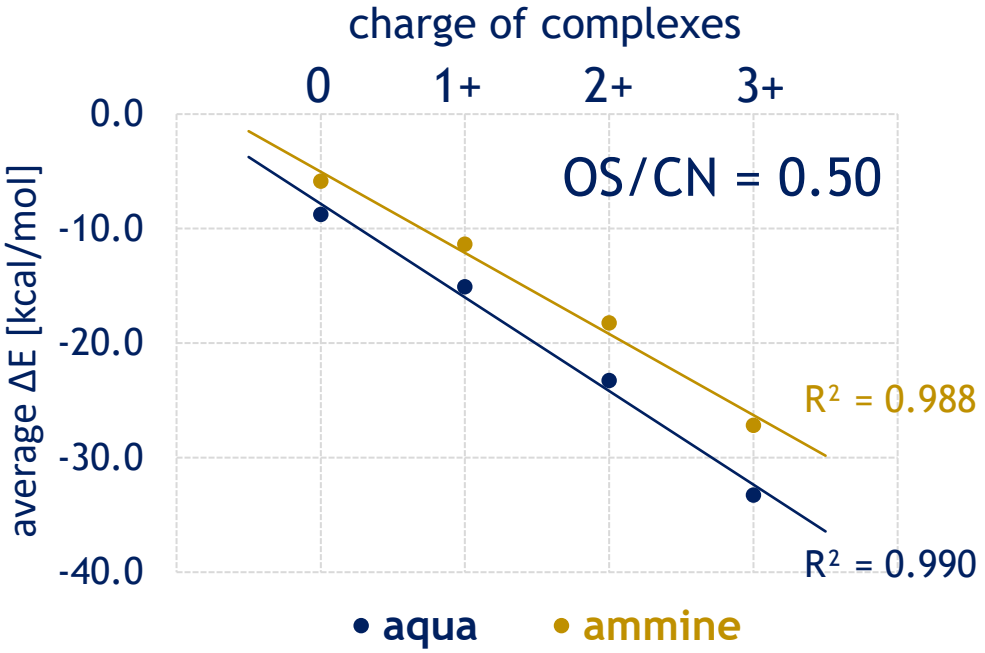


all complexes of the same type have very similar hydrogen bonds

Malenov *et al.*, *Dalton Trans.* 2025, **54**, 12754.

Interaction energy vs. charge of the complex

hydrogen bonds become stronger
with the increase in positive charge of the complex



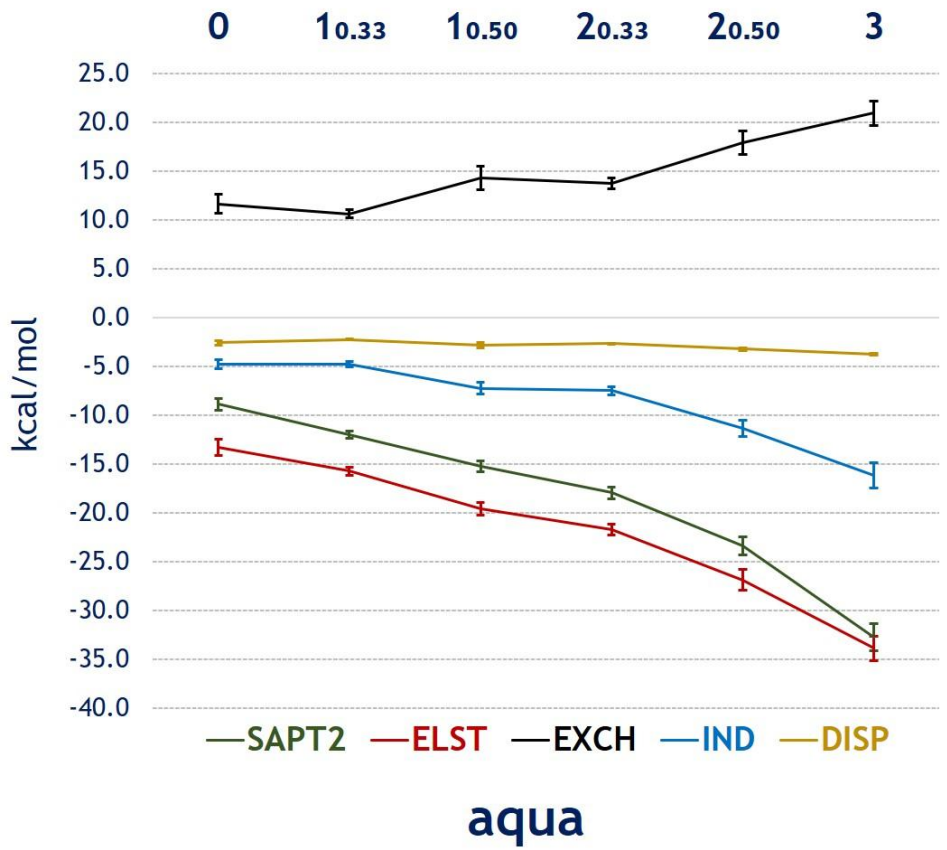
<u>linear correlation</u> between
interaction energy and charge
for complexes of the same OS/CN ratio (0.50)

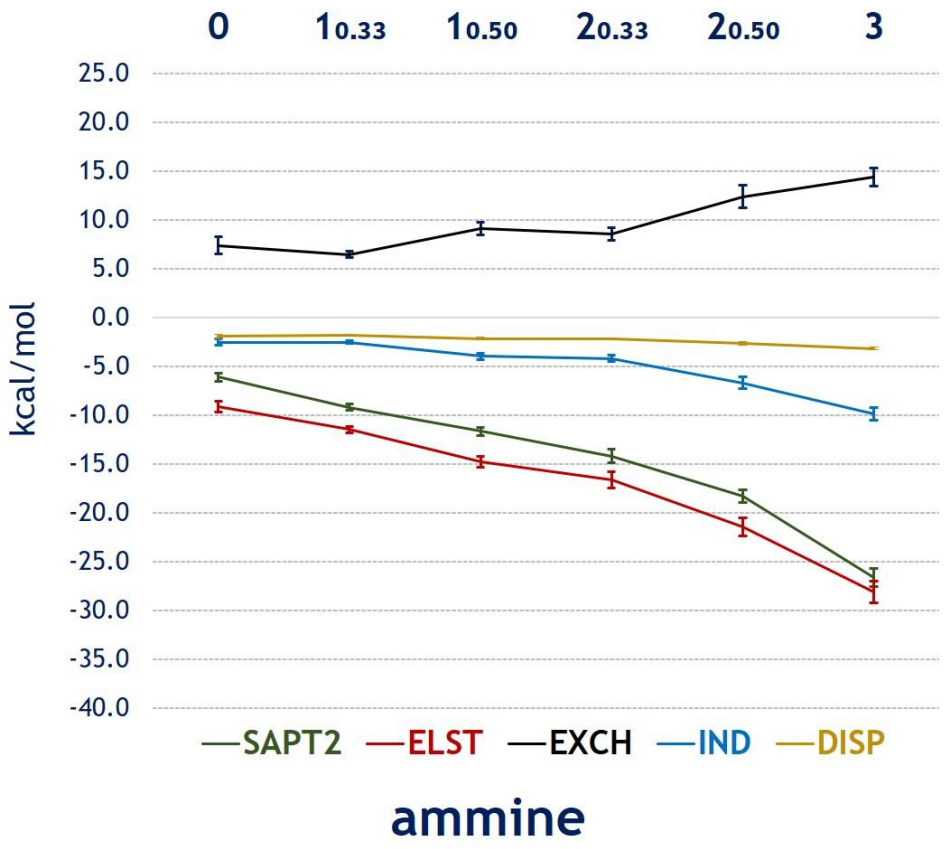
Malenov *et al.*, *Dalton Trans.* 2025, **54**, 12754.

Nature of hydrogen bonds of aqua and ammine metal complexes

SAPT2/def2-TZVP

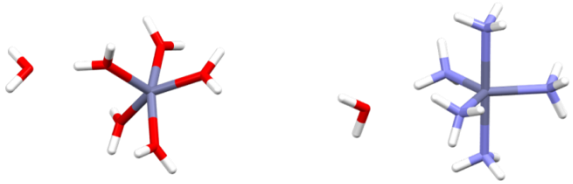
SAPT2 = ELST + EXCH + IND + DISP





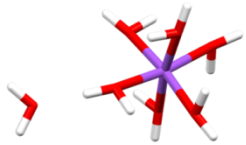
Malenov *et al.*, *Dalton Trans.* 2025, **54**, 12754.

Extending the data set with complexes of unusual composition

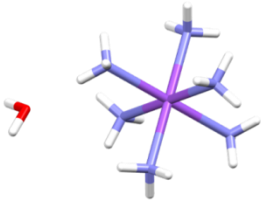


158
$[Zn(H_2O)_5]^{2+}\cdots H_2O$
OS/CN = 0.40
ΔE = -21.46 kcal/mol

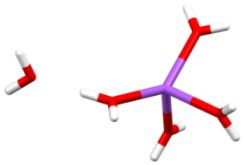
159
$[Zn(NH_3)_5]^{2+}\cdots H_2O$
OS/CN = 0.40
ΔE = -15.32 kcal/mol



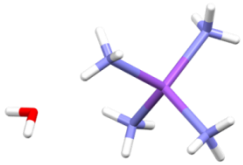
160
$[Na(H_2O)_6]^{+}\cdots H_2O$
OS/CN = 0.17
ΔE = -9.57 kcal/mol



161
$[Na(NH_3)_6]^{+}\cdots H_2O$
OS/CN = 0.17
ΔE = -6.01 kcal/mol

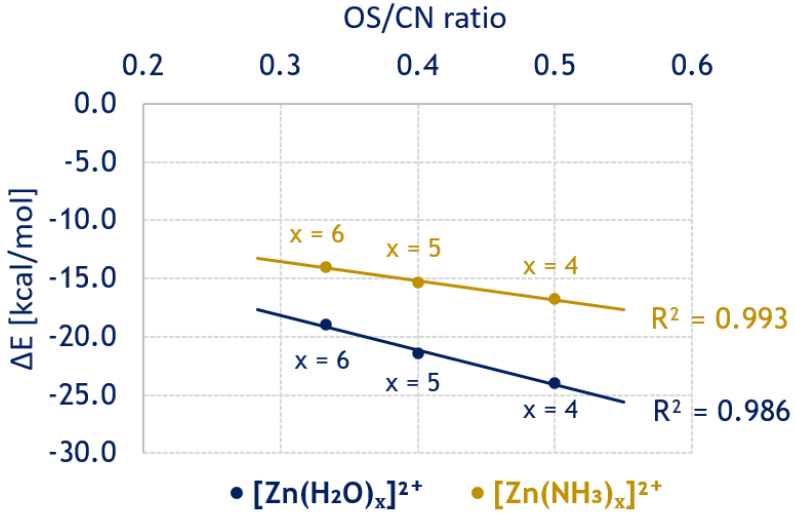


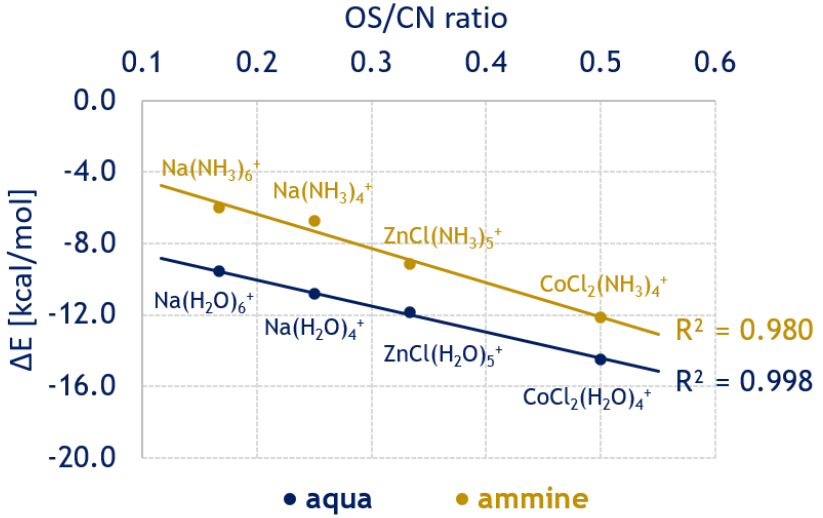
162
$[Na(H_2O)_4]^{+}\cdots H_2O$
OS/CN = 0.25
ΔE = -10.83 kcal/mol



163
$[Na(NH_3)_4]^{+}\cdots H_2O$
OS/CN = 0.25
ΔE = -6.75 kcal/mol

hydrogen bonds become stronger with the increase in OS/CN ratio





linear correlation between interaction energy and OS/CN ratio for complexes of the same charge

Malenov *et al.*, *Dalton Trans.* 2025, **54**, 12754.

Summary

Strength of hydrogen bonds is determined by the **charge of the complex** and **ratio of metal oxidation state and coordination number** (i.e. effective charge per ligand).
The influence of geometry, geometrical isomerism, and the presence of other ligands in the complex is very limited.

complex type	description	aqua	ammine
		kcal/mol	
0	neutral complexes	-8 to -10	-5 to -7
$1_{0.33}$	1+ charged octahedral complexes	-11 to -13	-8 to -10
$1_{0.50}$	all other 1+ charged complexes	-14 to -16	-11 to -12
$2_{0.33}$	2+ charged octahedral complexes	-17 to -20	-13 to -16
$2_{0.50}$	all other 2+ charged complexes	-22 to -25	-17 to -20
3	3+ charged complexes	-31 to -35	-25 to -29

All relationships are linear, making predictions of hydrogen bonds for "unusual" cases very reliable.

Predictions of hydrogen bond strength of metal complexes is possible by knowing their simple descriptors.

molecules

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Celebrating the 30th Anniversary
1996–2026

Computational Chemistry of Non-Covalent and Coordination Interactions

Special Issue Information

Within this Special Issue, we would like to welcome contributions that apply state-of-the-art computational methods, including quantum chemistry, density functional theory, molecular dynamics, as well as the cheminformatics approach, to study various types of noncovalent interactions. We welcome contributions related to interactions of both organic and inorganic compounds, and we particularly encourage works on noncovalent and coordination interactions in transition metal complexes. This Special Issue will focus on novel computational insights into hydrogen and halogen bonds, stacking interactions, and cation-π and anion-π interactions. We would also like to welcome contributions related to other new and exciting types of noncovalent interactions recognized in recent years.

Guest Editors

Dr. Dušan Malenov

Dr. Slađana Đorđević

Deadline for Manuscript Submissions: **31 December 2026**

► mdpi.com/si/271129

Keywords

- **noncovalent interactions**
- **coordination compounds**
- **hydrogen bonds**
- **metal complexes**
- **stacking interactions**
- **π-interactions**
- **computational chemistry**
- **density functional theory**

Special Issue

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