Copper(II) Coordination Compounds Correlations with Atomic Descriptors

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2020

Education

Universidad Nacional Autónoma de México (UNAM)

(4.5 year) Bs in Chemistry

Selected Courses:

- **Computational Chemistry, Quantum Chemistry II**

Other Courses:

- **Introduction to Deep Learning.**

Freie Universität Berlin (FUB)

Exchange Student

Selected Courses: .

- **Statistical Thermodynamics**

Research Experience

Institute of Chemistry, UNAM
Research Assistant
August 2018-Present
Advisor: Prof Dr. Fernando Cortés Guzmán

- Worked in 3 Projects
- Collaborated in a Published Paper:
  - DOI:10.1016/j.molstruc.2019.12748
- Presented Posters at three conferences
- Participated in Courses like "Introduction to Linux Systems" and "Introduction to Machine Learning"

QTAIM[1]

- Central Idea: atoms or group of atoms show intrinsic characteristics inside a molecule.
- Partitions ($\Omega \sim$ atoms): Done through $\rho(\mathbf{r})$ (Eq 1).
- $\rho(\mathbf{r})$ topology is dominated by the attractive forces of the nuclei.

$$\rho(\mathbf{r}) = N \int .. \int |\Psi(x_1, x_2, ..., x_N)|^2 d\omega dx_2, ..., dx_N \qquad (1)$$

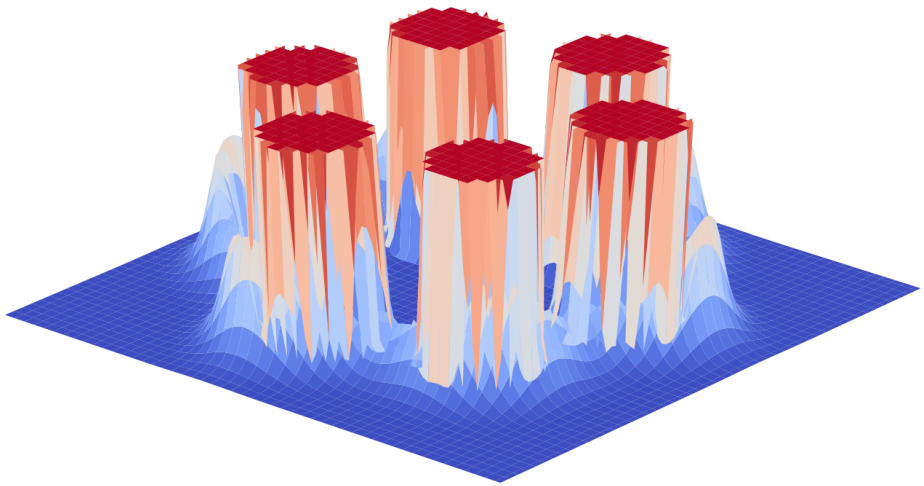


Figure 1: Relief map of $\rho(\mathbf{r})$ (benzene)

[1] R.F. W Bader. *Atoms in Molecules : A Quantum Theory*. eng. 1. publ. in paperback (with corr.) Oxford: Clarendon Press, 1994, XVIII, 438 S., [1] Bl. :, Ill., graph. Darst. ISBN: 0-19-855865-1.

Partitioning into Atoms[2]

- Atomic Partitioning $\rightarrow$ Atomic Properties.
- The average of an observable in a molecule is defined as Eq (2).

$$< \hat{A} >_{molecule} = \sum_{i}^{A} (N \int_{\Omega} \left\{ \int \frac{1}{2} [\Psi^* \hat{A} \Psi + (\hat{A}\Psi)^* \Psi] d\tau \right\} d\mathbf{r}) \quad (2)$$

- Electronic Populations:

$$N(\Omega) = \int_{\Omega} \rho(\mathbf{r}) d\mathbf{r} \quad (3)$$

- α or β Population:

$$< \psi_i(\mathbf{r}) | \psi_i(\mathbf{r}) >_{\Omega}^{\sigma} = \int_{\Omega} \psi_i^{\sigma *}(\mathbf{r}) \psi_i^{\sigma}(\mathbf{r}) d\mathbf{r} \quad (4)$$

[2] C.F Matta and R.J Boyd, eds. *Atoms in Molecules : An introduction; From Solid State to DNA and Drug Design*. eng. 1. publ. Harlow [u.a.]: Wiley-VCH, 2007.

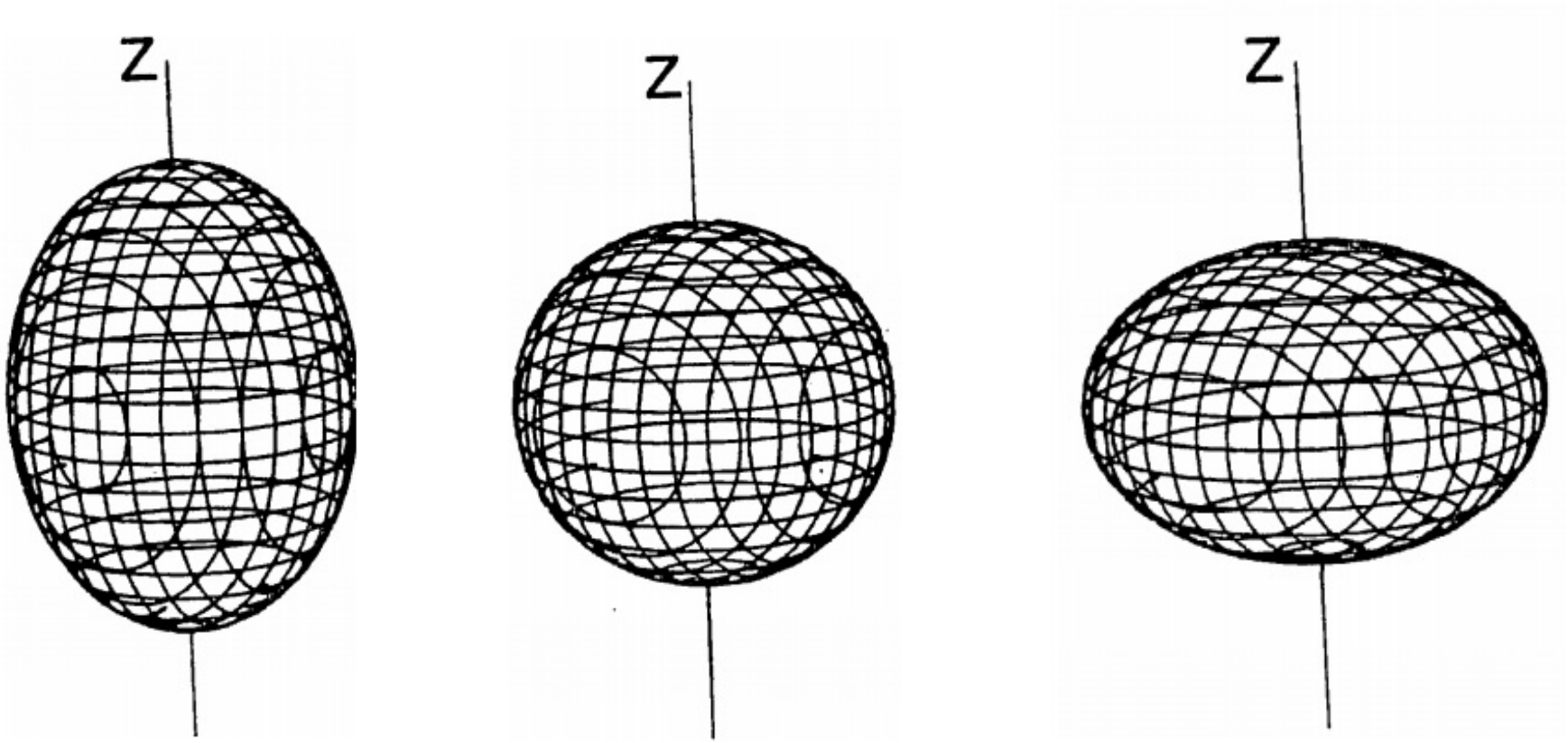
Atomic Quadrupole Moment[3]

- It is a symmetric tensor that measures the deviation of the atomic $\rho(\mathbf{r})$ from sphericity.

$$Q(\Omega) = -\frac{e}{2}\begin{pmatrix} Q_{xx} & Q_{xy} & Q_{xz} \\ Q_{yx} & Q_{yy} & Q_{yz} \\ Q_{zx} & Q_{zy} & Q_{zz} \end{pmatrix} \tag{5}$$

- $Q(\Omega)$ is a diagonalizable matrix with Q_1, Q_2, Q_3 diagonal elements.

[3] Matta and Boyd, *Atoms in Molecules : An introduction; From Solid State to DNA and Drug Design*.



(a) $Q_{zz} < 0$
Concentrated
Prolate

(b) $Q_{zz} = 0$
No Change
Sphere

(c) $Q_{zz} > 0$
Flattened
Oblate

Figure 2: Representation of quadrupolar polarizations[4]

[4] P.L. A Popelier. *Atoms in Molecules : An Introduction*. eng. 1. publ. Harlow [u.a.]: Prentice Hall, 2000, XIII, 164 S. :, Ill., graph. Darst. ISBN: 0-582-36798-0.

The Electronic Laplacian[5]

- In essence, $\nabla^2\rho(\mathbf{r})$ determines whether the functions is:
  - Concentrated:

$$\nabla^2\rho(\mathbf{r}) < 0 \tag{6}$$

  - Depleted:

$$\nabla^2\rho(\mathbf{r}) > 0 \tag{7}$$

- $\nabla^2\rho(\mathbf{r})$ has a topology of its own.
- Critical Points $\rightarrow \nabla^2(\nabla^2\rho(\mathbf{r}))u_i = \lambda_i u_i$
- Classification scheme:
  - r: rank; $\#\lambda|\lambda_i \neq 0$
  - s: signature ; $\sum sign(\lambda_i)$

[5] Popelier, *Atoms in Molecules : An Introduction*.

- Critical Points of an atom:
  - (3,+3) or vertices (V).
  - (3,+1) or edges (E).
  - (3,-1) or faces (F).
- Atomic graph: pictorial representation of a connectivity scheme.
- Euler's formula: $V + F - E = 2$

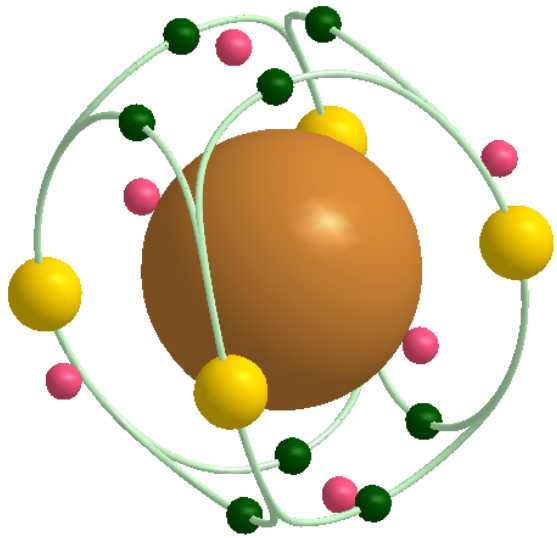


Figure 3: Critical Points for Copper(II)[6] : 4 V , 8 E y 6 F

[6] L. Gutiérrez-Arzaluz et al. "Origin of the Photoinduced Geometrical Change of Copper(I) Complexes from the Quantum Chemical Topology View". In: *Chemistry – A European Journal* 25.3 (2019), pp. 775–784. DOI: 10.1002/chem.201804596.

So Far:

- Topological Partiton(Ω) of $\rho(\mathbf{r}) \rightarrow N(\Omega), N_{\alpha}(\Omega), N_{\beta}(\Omega), Q(\Omega)$
- $\nabla^2\rho(\mathbf{r}) \rightarrow$ Basic and Acid Regions.
- $\nabla^2\rho(\mathbf{r})$ Topology $\rightarrow$ Atomic Graph.

This is study is based in Two Chemical Properties:

- $AGD \rightarrow$ Calculated.
- $Log\beta \rightarrow$ Experimental.

AGD Descriptor[7]

- "Atomic Graphic Descriptor".
- Mathematically defined as in Eq (8)

$$AGD = \sum \nabla^2 \rho(\mathbf{r})_{cc} - \sum \nabla^2 \rho(\mathbf{r})_{cd} \tag{8}$$

- Conceptual: describes the polarization in the valence shell of an atom and it is an approximation of the atom's hardness.

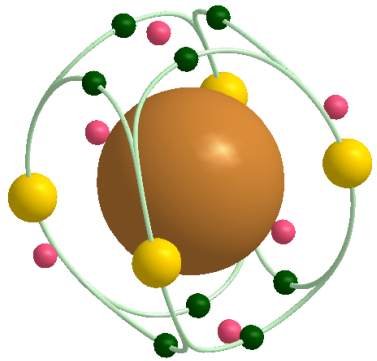


Figure 4: *AGD*: $\sum V(Yellow) - \sum F(Pink)$

[7] D.I Ramírez-Palma and F. Cortes-Guzman. *Tendencia periódica en las propiedades del Laplaciano de la Densidad Electrónica de Complejos de Metales de la primera serie del Bloque "d"*. Tesis Digital de UAEM: http://ri.uaemex.mx/handle/20.500.11799/14246. 2013.

Formation Constant of Copper(II)

- Formation constant: Thermodynamic equilibrium constant of a metal and a produced complex. (Eq 9)

$$\beta : Cu^{2+}_{(aq)} + nL_{(aq)} \rightleftharpoons CuL^{2+}_{n\,(aq)} \tag{9}$$

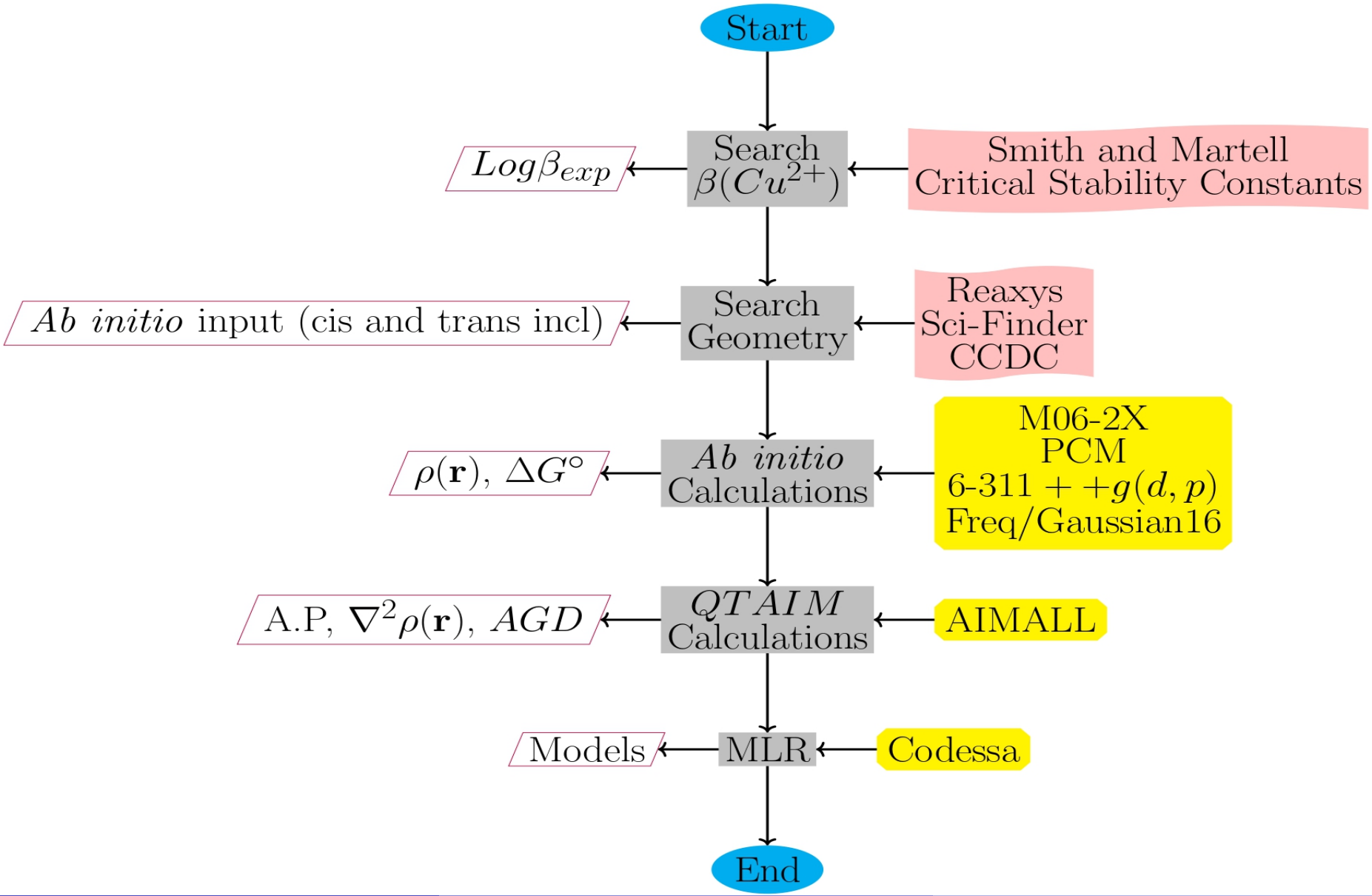
- Reported as $Log\beta$
- Compilations:[8] with diverse metals and ligands.
- Utility: To design and understand new complexes and its reactivity.
- Not all complexes can be reported or obtained experimentally

[8] R.M. Smith and A.E Martell. *Critical Stability Constants,Aminoacids*. Vol. 1. Plenum Press,New York and London, 1984; IUPAC. *The IUPAC Stability Constants Database*. discontinued. Academic Software: Yorks.

Aims

- To create a database of Cu(II) complexes with:
  - $Log\,\beta_{exp}$.
  - $Log\,\beta_{cal}$.
  - Geometry.
  - Atomic Properties (Cu).
  - $\nabla^2\rho(\mathbf{r})$ Information.
- To produce a predictive and explanatory model: $Log\,\beta_{exp} = f(Descriptors)$
- To produce a predictive and explanatory model: $AGD = f(Descriptors)$

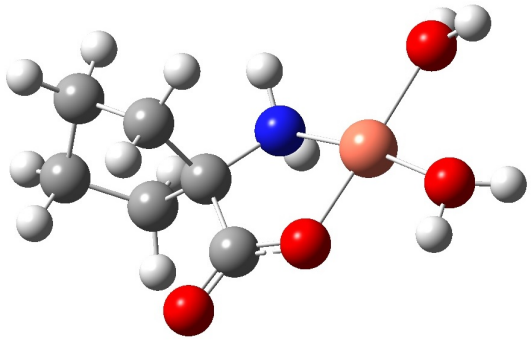
Method


Start
Search $\beta(Cu^{2+})$
$Log\beta_{exp}$
Smith and Martell Critical Stability Constants
Search Geometry
Ab initio input (cis and trans incl)
Reaxys Sci-Finder CCDC
Ab initio Calculations
$\rho(\mathbf{r})$, ΔG°
M06-2X PCM 6-311 + +$g(d,p)$ Freq/Gaussian16
QTAIM Calculations
A.P, $\nabla^2\rho(\mathbf{r})$, *AGD*
AIMALL
MLR
Models
Codessa
End

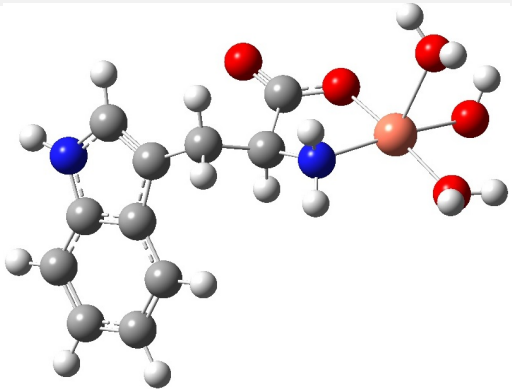
Database

Geometry	#
S.Pl	8
S.Py	11
Oct	39
Total	58

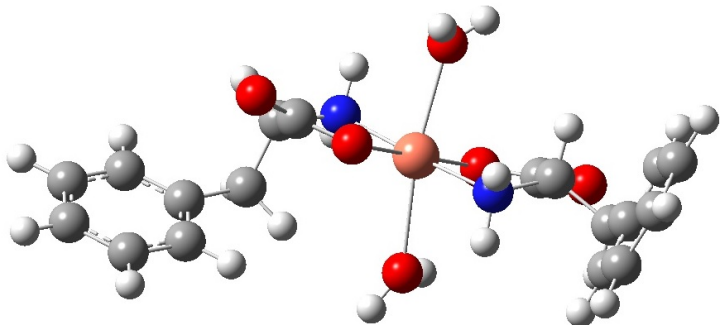
Table 1: Total Number of Molecules (20 ligands)



(a) Cycloleucine (S.Pl)



(b) Tryptophan (S.Py)



(c) Phenylalanine (Oct)

Figure 5: Some examples of the molecules in the database.

Calculated Formation Constant

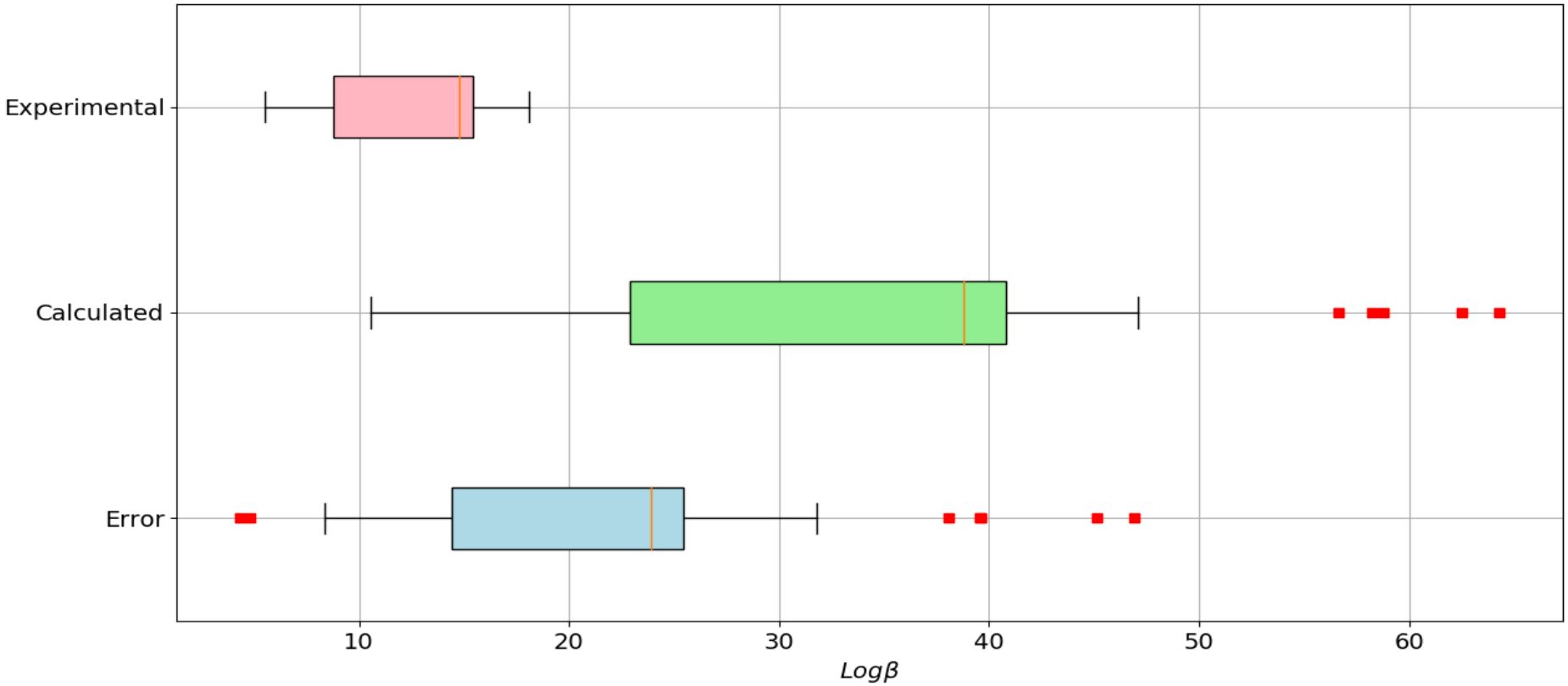


Figure 6: Box plots from *Experimental*, *Calculated*, and Absolute Error $Log\,\beta$

- Error range: 10-38 kcal/mol $\rightarrow$ Overestimation in $Log\,\beta_{cal}$

$Log\beta_{exp}$ and $Log\beta_{cal}$

For Cis Molecules:

$$Log\beta_{exp} = 0.310 Log\beta_{cal} + 1.8821 \quad (10)$$

For Trans Molecules :

$$Log\beta_{exp} = 0.305 Log\beta_{cal} + 1.9478 \quad (11)$$

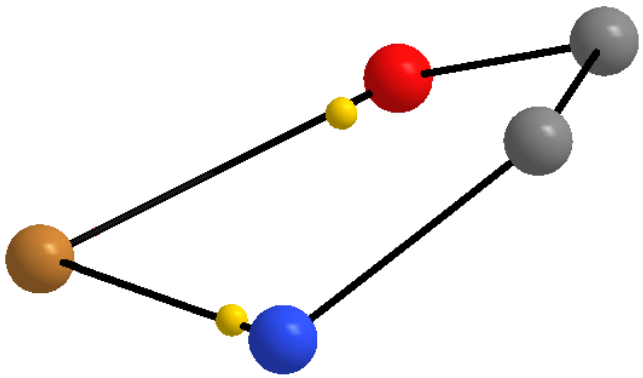
Table 2: Statistical Parameters of the Models

Eq	R^2	CV_{R^2}	|S.E|	$kcal/mol$	Molecules
10	0.903	0.891	1.145	1.54	36
11	0.910	0.897	1.119	1.50	36

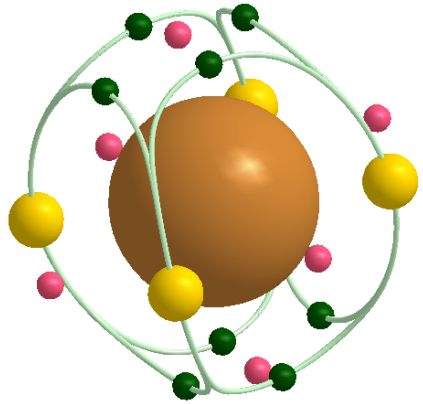
$Log\,\beta_{exp}$ Correlations

- For Cis Molecules:

$$Log\,\beta_{exp} = -0.337\boxed{\sum \nabla^2\rho(\mathbf{r})_{cc}(NO)}^{\{7a\}} - 0.567\boxed{\sum \nabla^2\rho(\mathbf{r})_{cc}(Cu)}^{\{7b\}} + 0.094\boxed{\sum \nabla^2\rho(\mathbf{r})_{cd}(Cu)}^{\{7b\}} + 89.841N(Cu) - 2656.510 \quad (12)$$



(a) Concentration CPs from O and N



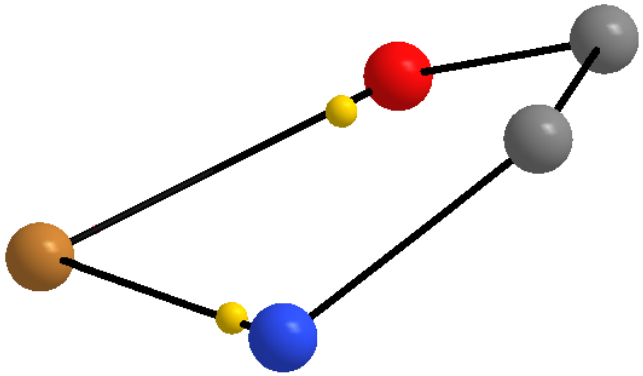
(b) Copper AG

Figure 7: $\nabla^2\rho(\mathbf{r})$ CPs considered

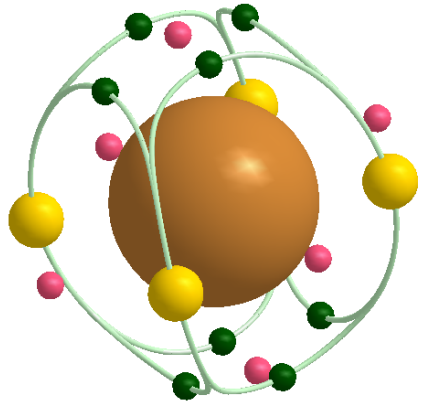
$Log\,\beta_{exp}$ Correlations

- For Trans:

$$Log\,\beta_{exp} = -0.314\boxed{\sum \nabla^2\rho(\mathbf{r})_{cc}(NO)}^{\{8a\}} - 0.507\boxed{\sum \nabla^2\rho(\mathbf{r})_{cc}(Cu)}^{\{8b\}} + 0.081\boxed{\sum \nabla^2\rho(\mathbf{r})_{cd}(Cu)}^{\{8b\}} + 88.369N(Cu) - 2656.510 \quad (13)$$



(a) Concentration CPs from O and N



(b) Copper AG

Figure 8: $\nabla^2\rho(\mathbf{r})$ CPs considered

$Log\,\beta_{exp}$ Models

Contributions to $Log\,\beta_{exp}$ from the descriptors:

- -0.314 $\sum \nabla^2\rho(\mathbf{r})_{cc}(NO)$ $\longrightarrow$ Positive $\longrightarrow$ Nucleophilic Bonded Atoms.
  - Concentration in $\sum \nabla^2\rho_{cc}(NO)$ $\longrightarrow$ Higher $Log\,\beta_{exp}$
  - $0.64 \sum \nabla^2\rho(\mathbf{r})_{cc}(NO) = \sum \nabla^2\rho(\mathbf{r})_{cc}(O)$

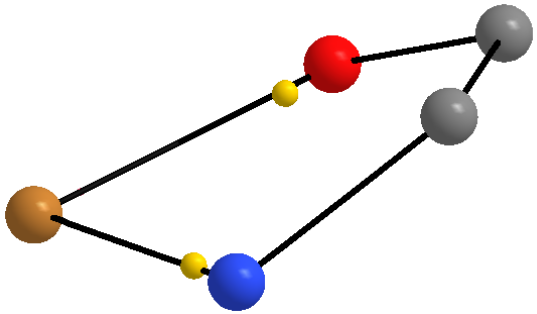


Figure 9: Concentration CPs from O and N

$Log\,\beta_{exp}$ Models

Contributions to $Log\,\beta_{exp}$ from the descriptors:

- $88.369N(Cu) \longrightarrow$ Positive $\longrightarrow$ Electronic population in Cu(II) (gain).
- -0.507 $\sum \nabla^2\rho(\mathbf{r})_{cc}(Cu)$ $\longrightarrow$ Positive $\longrightarrow$ Basicity from Copper(II).
- 0.0814 $\sum \nabla^2\rho(\mathbf{r})_{cd}(Cu)$ $\longrightarrow$ Negative $\longrightarrow$ Acidity from Copper(II).

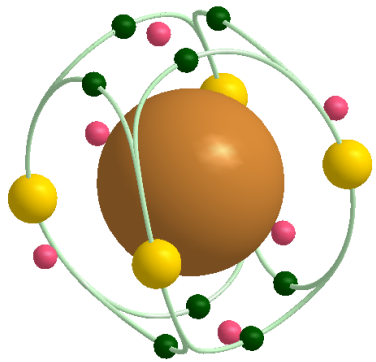


Figure 10: Copper(II) Atomic Graph

$Log\beta_{exp}$ Models

- In summary:

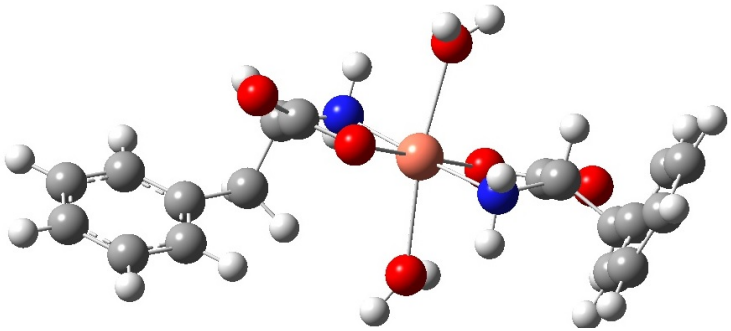
Table 3: Statistical Parameters of the Models

Descriptor	For	R^2	CV_{R^2}	|S.E|	$kcal/mol$	Molecules
$Log\beta_{cal}$	Cis	0.903	0.891	1.145	1.54	36
$Log\beta_{cal}$	Trans	0.910	0.897	1.119	1.50	36
QTAIM	Cis	0.954	0.935	0.762	1.02	37
QTAIM	Trans	0.948	0.933	0.802	1.08	37

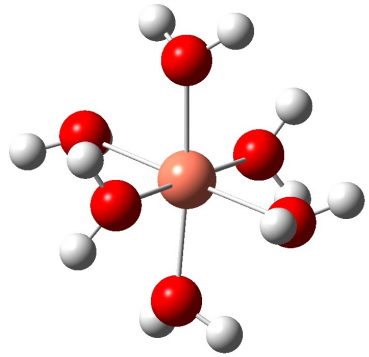
AGD Correlation

For all the Molecules in the Database:

$$AGD = -234.113\Delta N_{\alpha}(Cu) + 239.999\Delta N_{\beta}(Cu) + 11.653\Delta Q_1(Cu) - 142.693 \quad (14)$$



(a) $[CuL_n]$



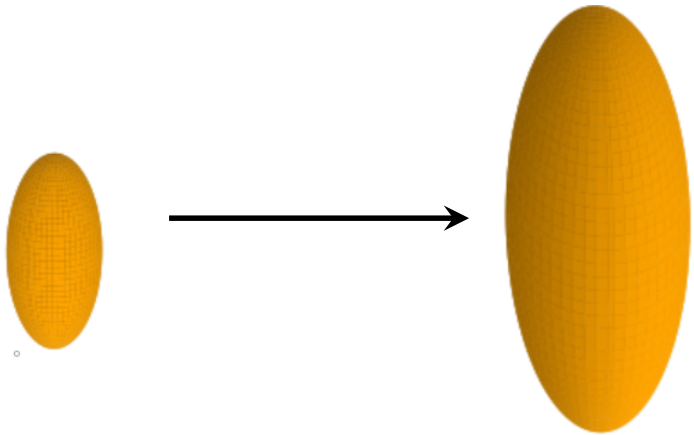
(b) $[Cu(H_2O)_6]^{2+}$

Figure 11: $\Delta \equiv [CuL_n]$-$[Cu(H_2O)_6]^{2+}$
Fig 11a- Fig 11b

Eq	R^2	CV_{R^2}	F	|S.E|	Molecules
14	0.914	0.889	177	0.782	54

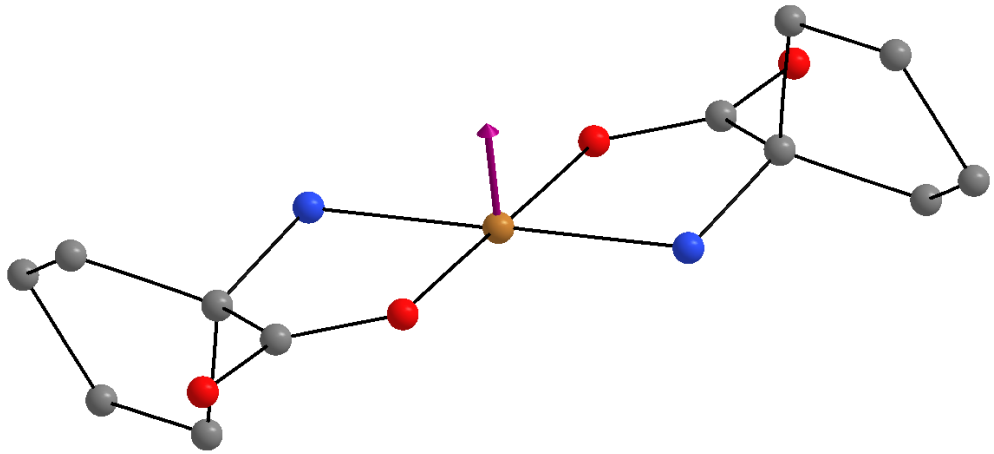
AGD Contributions

- 11.653 $\Delta Q_1(Cu) \longrightarrow$ Negative $\longrightarrow$ Shape of density.



(a) $[Cu(H_2O)_6]^{2+}$ $Q_1 < 0$

(b) $[CuL_n]$ $Q_1 < 0$



(c) Axial Direction

Figure 12: Representation of quadrupolar polarizations

AGD Models

Contributions to *AGD* from the descriptors:

- -234.113 $\Delta N_{\alpha}(Cu) \longrightarrow$ Negative $\longrightarrow \alpha$ Contribution
- 239.999 $\Delta N_{\beta}(Cu) \longrightarrow$ Positive $\longrightarrow \beta$ Contribution

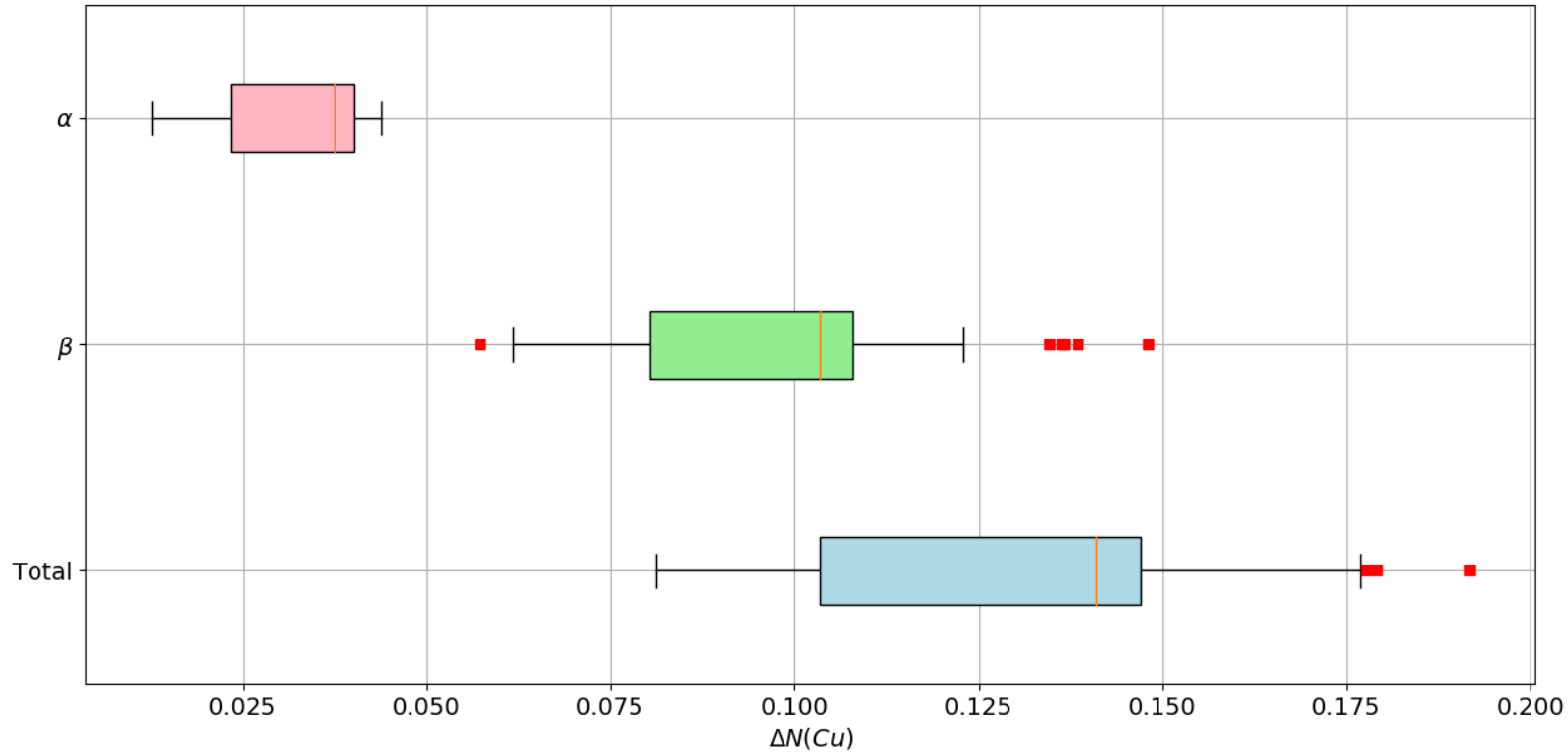


Figure 13: Box Plot from Changes in Electronic Population

In Conclusion

- $Log\beta_{exp}$ and $Log\beta_{cal} \rightarrow$ First approach but undescriptive and with a considerable |S.E|.
- $Log\beta_{exp} \rightarrow$ Tend to be higher as the bonded atoms increase their nucleophilic capacity and lower as the copper decreases its ability to accept electrons.
- $AGD \rightarrow$ Related with polarization terms; change in the form of the central atom electronic density and gains in the α,β populations.
- AGD and $Log\beta_{exp} \rightarrow$ Possible to create Models with the proposed Atomic descriptors.