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Supporting Information Placeholder

ABSTRACT: In the present work, we have calculated several DFT reactivity descriptors for the aminopoly carboxylates acids (APCs) at B3LYP/6311++G (d,p) levels of theory aiming to analyze its reactivity. Reactivity descriptors such as ionization energy, molecular hardness, electrophilicity, and condensed Fukui function local indices have been determined to predict the reactivity of APCs. The influence of the solvent was taken into account employing the CPCM model. The results indicate that the solvation slightly modifies the tendency of the reactivity of the APCs studied. On the other hand, we applied a global and local charge transfer partitioning model, which introduces two charge transfer channels (one for accepting electrons (electrophilic) and another for donating one (nucleophilic)), to the complexation reaction of a set of APC acids with transition metals (the Mn, Co and Ni target enlarged by Fe, Cu and Zn). The correlation between the charges obtained for the interaction between APC acids and transition metals stability constants provides support for their interpretation as measures of the electrophilicity and nucleophilicity of a chemical species, and, at the same time, allows one to describe the donation and back-donation processes in terms of the density functional theory of chemical reactivity. Also, the application of dual descriptors for this acids provides valuable information concerning the atoms in the reactants playing the most important roles in the reaction, and thus, helping to improve our understanding of the reaction under study.

1. INTRODUCTION

The contamination by heavy metals has been a serious problem in the last decades. The aminopolycarboxylates acids (APCs) have been widely used as ligands to capture the heavy metals. Therefore, the APC structures are also known for their good possibilities of heavy atom recovery. The chelation and dechelation of APCs complexes have been proposed as a novel green approach for heavy metal capture. However, the reactivity of the heavy metals with the APCs complexes is still the subject of several investigations[1-5].

Conceptual density functional theory is widely applied in various fields for understanding chemical reaction using the isolated properties of reactants [6-16]. It has been successfully exploited to unravel chemical reactivity and sites selectivity. To explain the chemical reaction without knowing a detailed knowledge of the reaction path, conceptual density functional theory uses global and local chemical descriptors [17-19] which contain reactivity information of the whole system.

Among chemical descriptors the most common ones involving global reactivity information are the chemical potential μ, the hardnessη and global softness S[20,21]. Another important local descriptors are the Fukui functions f(**r**)[10], dual descriptors[22,23] and the local softness s(r)[24]. These and other chemical reactivity indexes have been reviewed in the literature[18,25-28].

In the association reaction X + Y→ XY, one can show that the change in the energy involved can easily be expressed in terms of the electronegativities and hardnesses of the reacting species, by using the Parr and Pearson (PP) model[6,29]

Aiming to determine the charge-transfer mechanism, electrophilic or nucleophilic, prevailing in an association chemical reaction, Orozco-Valencia et al. presented recently a partitioning scheme for the number

of electrons exchanged in a reaction considering that both species accept and donate charge[30,31].

The main objective of this study is to explore the reactivity of the APC acids with respect to the complexation of some transition metals, namely Ni, Co and Mn, as presented in Figure 1.

Therefore, we carried out our study on three steps. The first one is the analysis of APCs reactivity by calculating different reactivity indices to determine which atoms in all of these acids plays the most important role in the reactions. In a second step, the charge transfer partition is calculated based on the global PP model, aiming to establish a correlation between the charge quantities transferred and the equilibrium constants. In the third step, the molecular orbitals of eight stable structures of EDTA are analyzed to understand the behaviour of APCs in these reactions. Besides, a natural population analysis (NBO) is carried out on all the nickel complexes.

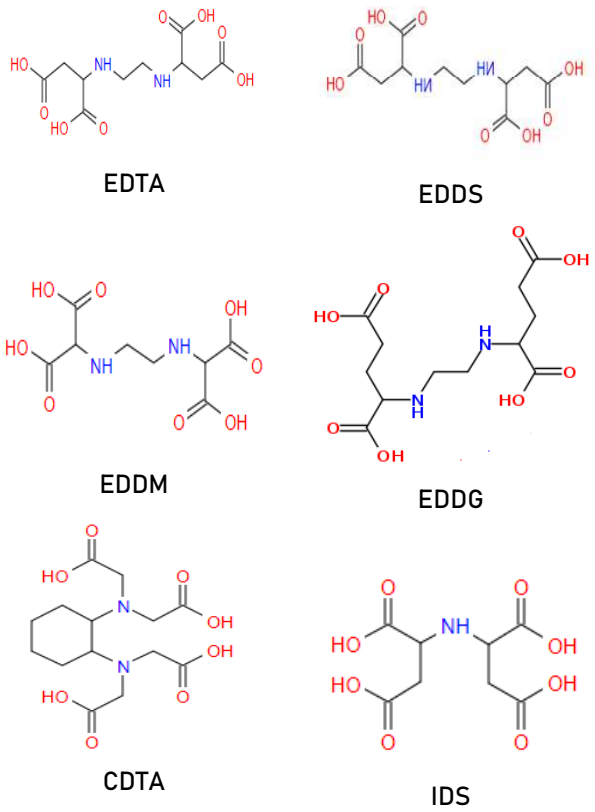


Fig. 1 the different aminopolycarboxylic acids with four carboxylic functions

The paper is organized as follows: after the description of computational methodology, we will study in the first part the relative reactivity prediction, the second part will be devoted to the dual descriptor and the Molecular Electrostatic Potentials, the last part will focus in the charge transfer between metal and ligand. The natural bond orbitals (NBO) analyses is also carried out and discussed. The paper ends with some concluding remarks

2. COMPUTATIONAL METHOD

All DFT calculations reported in this work were done employing the hybrid B3LYP functional[32–34] and the 6-311++G (d, p) basis set [35,36]. For transition metals, we use the LANL2DZ basis set. This standard and widely used functional is known to deliver rather good structures of organometallic systems (see, e.g. ref. [37–39]). A frequency analysis was done to confirm that all the stationary points located by the optimization procedure correspond to minima in the potential energy surface. Optimized APCs molecules in the gas phase were further re-optimized at the B3LYP/6311++G (d, p) level employing CPCM solvation model [40,41]in the aqueous medium. All the calculations reported here were performed with the Gaussian 09 package [42], visualized with the Gauss View [43] and Gabedit packages [44]. Electronic chemical potential and chemical hardness and softness were calculated from the frontier molecular orbital (FMO) eigenvalues. The natural bond orbital (NBO) calculations have been performed for each reactant using the NBO 3 program[45] interfaced with Gaussian 09 [42].

Global reactivity descriptors indices such as electronegativity, electronic chemical potential (μ)(which is equal to the negative of the electronegativity), hardness (η), electrophilicity index (ω) [12,18,25–28,46], are calculated according to Koopmans' theorem as follow:

$$\mu \approx -\frac{1}{2}(I + A) \qquad (1)$$

where $I = -E_{HOMO}$ and $A = -E_{LUMO}$

$$\mu \approx \frac{\varepsilon_{LUMO} + \varepsilon_{HOMO}}{2} \qquad (2)$$

$$\eta \approx I - A \qquad (3)$$

$$\eta \approx \varepsilon_{LUMO} - \varepsilon_{HOMO} \qquad (4)$$

The global softness (S) is defined as the reciprocal hardness as follow:

$$S = \frac{1}{\eta} \qquad (5)$$

The absolute electronegativity (χ) is defined as[20]

$$\chi = -\mu \qquad (6)$$

The nucleophilicityindex[47] is calculated referred to tetracyanoethylene (TCE) is given by:

$$N_u = \varepsilon_{HOMO(Nuc)} - \varepsilon_{HOMO(TCE)} \quad (7)$$

where: $\varepsilon_{HOMO(TCE)} = -9.367eV$ [47] (In our computational conditions (same functional, same basis set, same solvent), one gets $\varepsilon_{HOMO(TCE)}$=-9.303 eV). The tiny shift does not affect the trends, evidently.

The global electrophilicity index ω was introduced by Parr[8,18,25] and it is calculated using the electronic chemical potential μ and the absolute hardness η:

$$\omega = \frac{\mu^2}{2\eta} \approx \frac{(I+A)^2}{8(I-A)} \quad (8)$$

Accordingly, ω measures the ability of a species to accept electrons. Thus, low values of ω indicate a good nucleophile while high values characterize good electrophiles.

Relative reactivity prediction

The relative reactivity of substitutions has been rationalized using the global nucleophile index proposed by Domingo et al.[47]defined according to equation 7. As is well known, the HOMO and LUMO frontier molecular orbitals provide understanding in the efficiency in the interaction between chemical reactants: A high value of the quantum chemical descriptor ε_{HOMO} favors the molecule to electron donation, whereas a low value of ε_{LUMO} favors the electron capture by the molecule. The hardness helps us to characterize the chemical reactivity and the kinetic stability of the molecular product.

From Table 1, the results reveal that all of the acids have strong gap values, which indicates good stability. On the other hand, by examining the values of global nucleophilicity index, we note that the CDTA ligand has the greatest nucleophilic index (N_u= 3.727, 3.545 in gas, solvent phases, respectively) compared to the other ligands.

The analysis of HOMO energy, which acts as an electron donor[48], indicates a tendency for the molecule to donate an electron to the appropriate metal as an electron acceptor. Let us recall that a good nucleophile has high chemical potential and a high value of HOMO energy, and has low electrophilicity index ω. This tendency is:

CDTA>EDTA>EDDM□>EDDS>EDDG>IDS

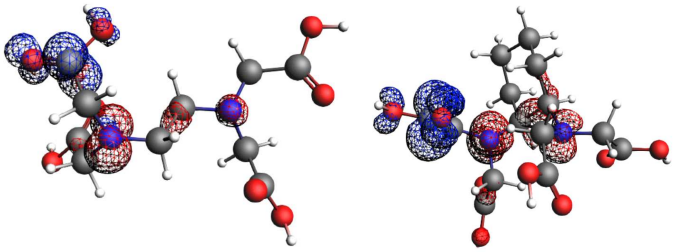
Table 1: Calculated quantum chemical parameters and global reactivity descriptors of the studied APCs ligands (italic values for solvated species) in eV.(eV^{-1} for S)

Ligand	E_{HOMO}	E_{LUMO}	Nu	μ	X	η	S	ω	ΔNmax
CDTA	-5.641/*-5.823*	-0.979/*-1.017*	3.727/*3.545*	-3.310/*-3.420*	3.310/*3.420*	4.662/*4.805*	0.214/*0.208*	1.174/*1.217*	0.710/*0.712*
EDTA	-6.040/-6.*548*	-0.572/*-0.646*	3.328/*2.820*	-3.306/*-3.597*	3.306/*3.597*	5.468/*5.902*	0.183/*0.169*	0.999/*1.100*	0.604/0.609
EDDS	-6.772/*-6.952*	-0.859/*-0.769*	2.592/*2.416*	-3.815/*-3.861*	3.815/3.861	5.913/*6.182*	0.169/*0.162*	1.231/*1.205*	0.645/*0.624*
EDDM	-6.773/*-6.905*	-0.927/*-0.999*	2.595/*2.462*	-3.850/*-3.952*	3.850/*3.952*	5.846/*5.906*	0.171/*0.169*	1.268/*1.322*	0.658/*0.669*
EDDG	-7.061/*-6.736*	-0.953/*-0.674*	2.306/*2.632*	-4.007/-3.705	4.007/*3.705*	6.108/*6.062*	0.164/*0.165*	1.314/*1.132*	0.656/*0.611*
IDS	-7.126/*-6.871*	-0.993/*-0.894*	2.242/*2.497*	-4.060/*-3.882*	4.059/*3.882*	6.133/*5.977*	0.163/*0.167*	1.343/*1.261*	0.662/*0.649*

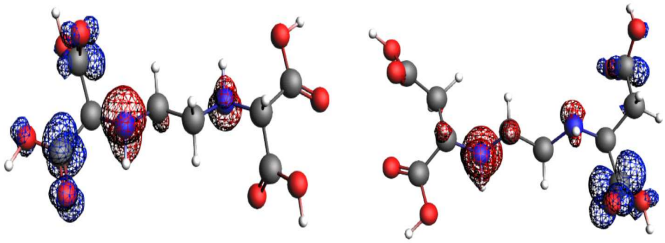
It can be observed from Table1 that the global hardness η is slightly modified when the solvent is taken into account with respect to the gas phase. One of the reasons is that a polar solvent, such as water, could stabilize the charged species with respect to the gas phase, therefore modifying the value of η without having a direct implication on the reactivity of the APCs.

3. DUAL DESCRIPTOR

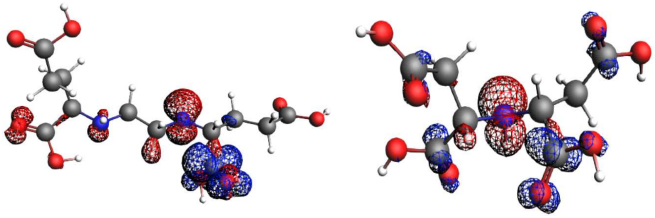
The dual descriptor (DD) Δf(**r**), introduced by Morell[22,23] measures how the absolute hardness changes with an external potential change. Typically, this occurs when reactants approach each other during a bimolecular reaction. The DD can also be defined as the second derivative of the electron density with respect to the number of electrons, and



EDTA CDTA



EDDM EDDS



EDDG IDS

Figure 2. Dual descriptors of the 6 APCs (isocontours = 0.005au)

it can be calculated as the difference between the electrophile and nucleophile Fukui functions:

$$\Delta f(\boldsymbol{r}) = f^{+}(\boldsymbol{r}) - f^{-}(\boldsymbol{r}) \qquad (9)$$

Accordingly, where Δf(r) > 0, nucleophilic attack is favored rather than electrophilic attack, whereas if Δf(**r**) < 0, point **r** favors electrophilic attack. Consequently, positive values of Δf(**r**) point out electrophilic regions within a molecular topology, whereas negative values of Δf(**r**) highlight nucleophilic regions. Maps of the dual descriptors for each APCs acids are shown in Fig. 2.Negative (Δf(**r**) < 0) regions are colored in red, whereas positive (Δf(**r**) > 0) regions are blue. As expected, the negative regions of the DD are located on the nitrogen atoms, indicating that any electrophilic attack would take place on the nitrogen lone pairs. This is expected because the HOMO (and HOMO-1) should be located on the lone pairs of the nitrogen(s). We will discuss this point below.

4. MOLECULAR ELECTROSTATIC POTENTIALS (MEP)

MEPs are also used to investigate the chemical reactivity of a molecule. Former works on the application of MEP to chemical facts[49-52] highlighted the possibilities of MEP in the interpretation of reactivity. This is especially important for the identification of the reactive sites of nucleophilic or electrophilic attack.

The MEP surface shows the charges distribution in the different acids. The electrostatic potential increases in the following order: red <yellow< green <blue. The negative regions are red and the blue ones indicate positive regions. The resulting overall MEP of the different APCs (Figure 3) shows that the red regions are located on the oxygen atoms (C=O) indicating that those oxygen atoms will be the preferred sites for electrophilic attack.

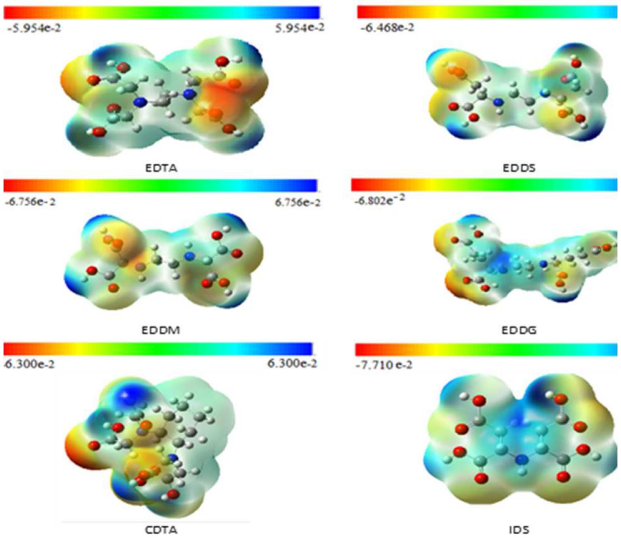


Fig. 3.Electrostatic potentials mapped on the electron density surface

Figure 3. Electrostatic potentials mapped on the electron density surfaceof the 6 APCs

5. MO OCCUPATION

The MOs diagrams show clearly that the HOMO and HOMO-1 (for the five chelating ligands holding two nitrogens) are typically the orbitals holding the lone pairs of the nitrogen(s), as expected. Since several stable conformations can be optimized, it is interesting to see, among these conformations, if these lone pairs are identically occupied by the two orbitals or if the HOMO is more localised on a given nitrogen, whereas the HOMO-1 is in the majority localised on the other nitrogen. Table 2 reports the case of 8 different structures of EDTA for which we can observe that the energy gap between the HOMO and HOMO-1 is neither related to the stability of the structure, nor to a localisation/delocalisation on the nitrogens.

Table 2: The calculated energy gap for 8 different structures of EDTA (eV)

Structure number	Total Bonding Energy kcal/mol	"Gap" HOMO-HOMO-1	HOMO-1 π N12	HOMO-1 π N11	HOMO π N12	HOMO π N11	HOMO-1 eigenvalue	HOMO eigenvalue
1	-5040.48	0.282	0	56	61	2	-5.853	-5.571
2	-5041.89	0.791	51	13	7	46	-5.896	-5.105
3	-5041.97	0.518	38	23	22	38	-5.913	-5.395
4	-5042.84	0.709	53	8	9	49	-5.967	-5.258
5	-5043.41	0.349	23	34	36	24	-5.42	-5.071
6	-5044.96	0.515	4	50	60	4	-5.911	-5.396
7	-5045.29	0.549	12	46	47	12	-5.497	-4.948
8	-5047.93	0.582	10	49	43	12	-5.472	-4.890

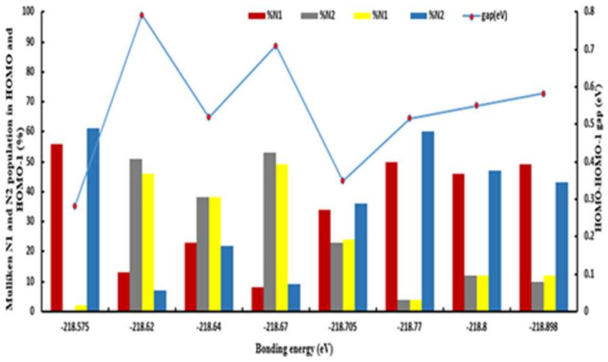


Fig.4 HOMO-(HOMO-1) gap *vs* bonding energy among EDTA structures (kcal/mol).The N populations are that of HOMO (left) and HOMO-1 (right) for N1 and N2..

Surprisingly, there is no correlation between the stability of the conformer and the localization of the lone pairs on the two nitrogens. The localization, here measured by the Mulliken population of nitrogens in the HOMO and HOMO-1, is illustrated in Fig. 4. It clearly shows that the localization is maximum on a given nitrogen in the HOMO (and consequently maximum for the other nitrogen in the HOMO-1) for the most stable structure, but also for least stables ones (among the calculated structures). On the contrary, a few structures exhibit rather equally distributed lone pair electrons on the nitrogens among the HOMO and HOMO-1. This large variation of the electron density among the different conformers lets expect an easy transformation towards more or less reactive conformations.The reactivity is probably *in fine* not necessarily related to the electronic properties of the most stable conformation of the ligand, but to one conformation exhibiting a more localized density on one nitrogen in the HOMO, leading to a starting complexation process. That will involve a geometry deformation relocalizing the density on the second nitrogen on the ligand fragment within the complex formation. A full analyse of the complexation process is out of the scope of the present work.

6. METAL-LIGAND NET CHARGE TRANSFER

In the density functional theory of chemical reactivity[21,53] , the charge transfer terms are related to the interaction energy as part of a covalent contribution. Orozco-Valencia et al.[30,31] have provided expressions for the transfer of charge ΔN and of energy difference ΔE which complete the formation of a complex between an acid A and a base B, namely:

$$\Delta E = \mu \Delta N + \frac{1}{2}\eta(\Delta N)^2 \qquad (10)$$

Considering the interaction between two systems X and Y, and analyzing the process of charge transfer occurring between these two species, the charge

transfer between X and Y is given by the expression below:

$$\Delta N_X = N_X^{Ele} + N_X^{Nuc} \quad (11)$$

where N_X^{Ele} is the electrophilic component, representing the charge transferred in the electrophilic channel of reactant X, which means that X is accepting electrons (it must take positive value). $N_X^{Nuc}$is the nucleophilic component, which means thatN_X^{Nuc} is the charge transferred through the nucleophilic channel of X, X being then donating electrons (it must be negative). There are similar equations for reactant Y where the roles are inverted in accordance with the charge conservation. In general, when the two reacting systems X and Y are neutral, the directions of charge transfer agree with the chemical potential differences. The expressions to calculate the amount of electrons transferred in these two channels are:

$$\Delta N_X^{Ele} = \frac{I_X - A_Y}{2(\eta_X + \eta_Y)} = -\Delta N_Y^{Nuc} \quad (12)$$

$$\Delta N_X^{nuc} = \frac{A_X - I_Y}{2(\eta_X + \eta_Y)} = -\Delta N_Y^{Ele} \quad (13)$$

When the charge transfer increases, the interaction between the metal and the ligand is stronger[36].According to the expressions 12 and 13, one can determine the back-donation and the donation between metals and APCs acids respectively. To apply these relationships to our systems, we need first to calculate the first vertical ionization potential I, and the vertical electron affinity A defined in eq(1), of the APCs acids, here considered as species X, and of the metal identified as species Y. The average chemical potential and the hardness η, of both species are collected in Table 3

Table 3. Ionization potential, electron affinity, chemical potential and hardness, in eV, for a set of APC ligands, and Mn, Co and Ni atoms.

	I_Y	A_Y	μ_Y	η_Y
Mn	4.837	3.016	-3.926	1.821
Co	5.886	3.195	-4.540	2.691
Ni	4.884	3.242	-4.051	1.641
	I_X	A_X	μ_X	η_X
CDTA	5.641	0.979	-3.310	4.662
EDTA	6.040	0.572	-3.306	5.468
EDDS	6.772	0.859	-3.815	5.913
EDDM	6.773	0.927	-3.850	5.846
EDDG	7.061	0.953	-4.007	6.108
IDS	7.126	0.993	-4.059	6.133

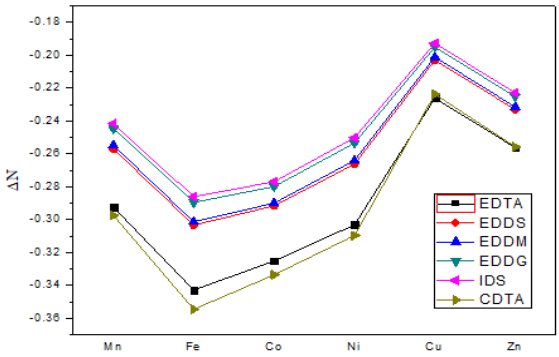


Fig 5. The variation of charge transfer according to metals

According to the results plotted in Fig. 5, it can be seen that the charge transfer for the same metal follows the descending order: IDS<EDDG< EDDM< EDDS< EDTA<CDTA. It is the same order as that we obtained for the HOMO eigenvalue and the electrophilicity index

We have gathered in Table 4 the calculated values ofΔN_X,ΔN_X^{ele} and ΔN_X^{nuc} obtained from Eq. (11), (12) and (13), respectively. We have also reported the experimental values of stability constants log K corresponding to the (APCs) metal complexes.

A negative sign of ΔN_X^{nuc} indicates that charge is transferred from the ligand to the metal, while a positive value of ΔN_X^{ele} indicates the opposite direction, the charge is transferred from the metal to the ligand. Their absolute values indicate the amount of charge transferred through the two channels.

Table 4. Net charge (Eq.11), electrophilic charge (Eq.12), nucleophilic charge(Eq.13), log K experimental values[54]

	Metal	ΔN_X^{ele}	ΔN_X^{nuc}	ΔN_X	log K
	Mn	0.2074	-0.2925	-0.0851	13.9
EDTA	Co	0.1747	-0.3252	-0.1505	16.31
	Ni	0.1967	-0.3032	-0.1055	18.62
	Mn	0.2428	-0.2571	-0.0143	9.0
EDDS	Co	0.2082	-0.2917	-0.0835	14.02
	Ni	0.2336	-0.2663	-0.0327	16.7

	Mn	0.2450	-0.2549	-0.0099	8.45
EDDM	Co	0.2099	-0.2900	-0.0801	12.20
	Ni	0.2358	-0.2641	-0.0283	14.5
	Mn	0.2550	-0.2449	0.0101	6.74
EDDG	Co	0.2200	-0.2799	-0.0599	10.62
	Ni	0.2464	-0.2535	-0.0071	13.04
	Mn	0.2583	-0.2416	0.0167	7.3
IDS	Co	0.2227	-0.2770	-0.0543	10.5
	Ni	0.2497	-0.2502	-0.0005	12.2
	Mn	0.2024	-0.2975	-0.0951	17.5
CDTA	Co	0.1661	-0.3336	-0.1675	19.7
	Ni	0.1902	-0.3097	-0.1195	20.2

Therefore, the stronger electron-withdrawing ligands correspond to those with largerΔN_X^{ele}, and the stronger electron-donating groups correspond to those with larger absolute value ofΔN_X^{nuc}.

Figure 6 shows the overall correlation between ΔN_X^{nuc} and the log K values of metal complexes, using Eqs. (10), (11) and (12), one can show that:

$$\Delta N_X^{ele} = \frac{1}{2}\Delta N_X + \frac{1}{4} \qquad (14)$$

and:

$$\Delta N_X^{nuc} = \frac{1}{2}\Delta N_X - \frac{1}{4} \qquad (15)$$

This approach provides a tool for measuring the capacity of the electron donor or the nucleophilicity of, in this case the APC ligands withΔN_X^{nuc}, and the electron acceptor capacity or electrophilicity with ΔN_X^{ele}, of Mn, Co and Ni. From calculated results in Table 4, a good linear correlation is found by plotting the equilibrium constants of the complexation reaction with the amount of electrons transferred through the nucleophilic channel(see Figure 6).The same correlation is found for the amounts of electrons transferred, as defined in equations 11 and 14 [30].

It is important to note that the electron acceptor-donor properties measured with ΔN_A^{nuc} and ΔN_A^{ele} clearly depend on the chemical nature of the APCs.

The APCs ligands have electron donator atoms, such as the four O atoms and two N atoms which have the greatest electrodonation capacity, so that they give more charge to Mn, Co and Ni.

These ligands can be arranged according to the absolute values ofΔN_X^{nuc} sorting them in decreasing order of their nucleophilicity, one gets: CDTA> EDTA> EDDS> EDDM> EDDG> IDS, (and the opposite trend for the values of ΔN_A^{ele}). This is the order already found in Table 1.

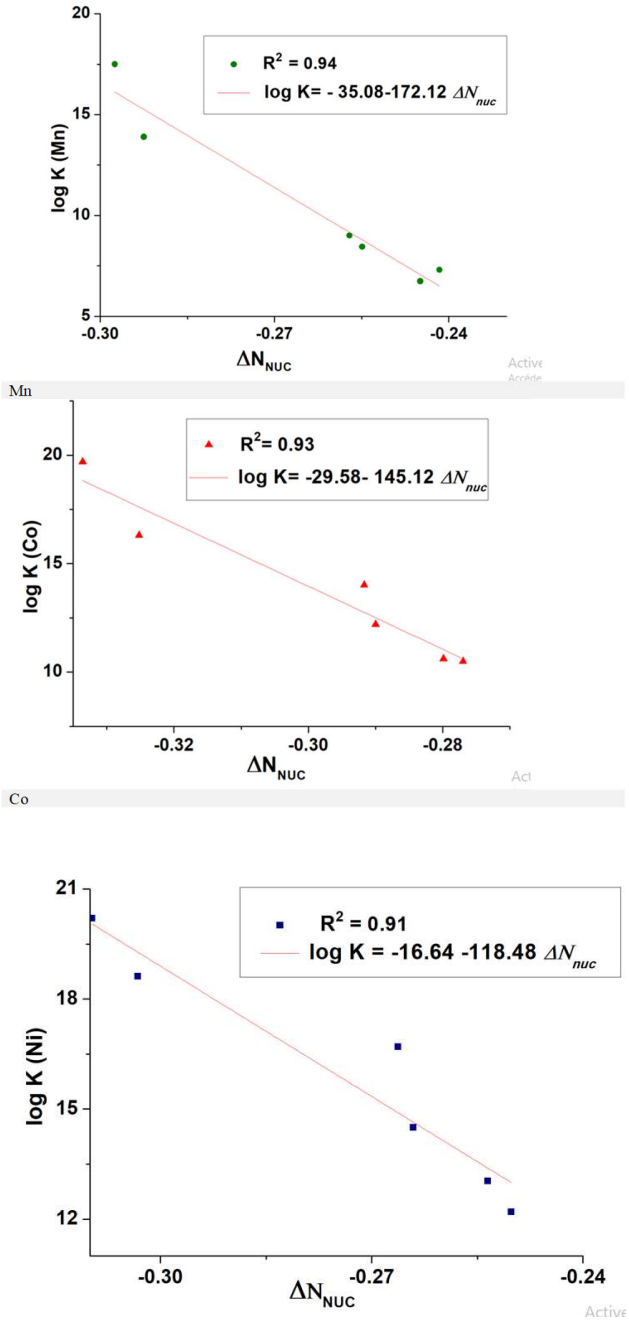


Fig. 6.. The equilibrium constant of the complexation reaction between APCs and Mn, Co, and Ni metals with the amount of electron transfer through the nucleophilic channel using values reported in Table 4.

5. NBO NICKEL COMPLEXES ANALYSIS

To highlight the donation and the back-donation of the metal-ligand, the NBO analysis is applied to the nickel complexes.

The second order perturbation analysis of the Fock matrix between the APCs and the transition metals are reported in Tables S.2-7 in SI.The NBO results show that, in those complexes, there is the interaction between σ (N-C), σ (C-O), LP (N) and LP (O) of the ligand with the nickel lone pair LP (Ni)and the weak interaction with Ry* (Ni).However, a weak retrodonation from the Ni atom lone pairs to the ligand is noted except for the EDDS complex case, where a larger retrodonation is observed between LP* (Ni) and Ry* (C), σ* (C-O)(see Table S.6. in SI).Therefore, the APCs complexes stabilization is due to the intramolecular charge transfer resulting from the N-C, C-O bonds as well as the nitrogen and oxygen atoms lone pairs of ligand to the nickel atom lone pairs.

6. CONCLUDING REMARKS

The results obtained in this work shed light on the driving forces in the complexation reactions of transition metals by APCs. MEPs and DD approaches allow one to clearly identify the atoms involved in the complexation reactions. The values of ΔN_A^{nuc} and ΔN_A^{ele} derived through the application of partitioning schemes provide information on the electrophilicity and nucleophilicity of the chemical species. Interestingly, we have found good correlations between these quantities and the complexation equilibrium constants for these metals.

Finally, the donation σ and the back-donation π, which is clearly framed in orbital language, can be reinterpreted in terms of charge transfer processes framed in the approach of the DFT for chemical reactivity[26,55], and expressed in terms of important chemical concepts like chemical potential (electronegativity) and hardness of interacting species .The NBO results show that, the APCs complexes stabilization is due to the intramolecular charge transfer resulting form the sigma N-C, C-O bonds as well as the nitrogen and oxygen atoms lone pairs of ligand to the nickel atom lone pair. However, a weak retrodonation from the Ni atom lone pairs to the ligand is noted, the EDDS complex case excepted, where a more important retrodonation is observed between LP* (Ni) and Ry* (C), σ* (C-O).

ACRONYMS OF THE APCs

EDTA: Ethylenediaminetetraacétic acid
EDDS: Ethylenediamine-N,N'-disuccinic acid
EDDM: Ethylenediiminopropanedioic acid
EDDG: Ethylenediamine-N,N'-diglutaric acid
CDTA: Cyclohexanediaminetetraaceticacid
IDS: Iminodisucciniqueacid

ASSOCIATED CONTENT

Supporting Information

Table S1: structures and atom numbers

Tables S2-S7: NBO charges in the 6 complexes

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Notes

Any additional relevant notes should be placed here.

Acknowledgments:

The authors gratefully acknowledge the GENCI/CINES for HPC resources/computer time (Project cpt2130), as well as the PSMN of the ENS-Lyon for computing resources.N.R acknowledges HPC UFMC 1, Unité de Recherche de Chimie de l'Environnement et Moléculaire Structurale, CHEMS, Université FrèresMentouri Constantine 1,for support and computingresources.

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