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Ligand(s)-to-Metal Charge Transfer as a Factor Controlling the Equilibrium Constants of Late First-row Transition Metal Complexes: Revealing the Irving-Williams Thermodynamical Series

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A unified relationship between the experimental formation constants of versatile ligand complexes of the late transition series first-row bivalent metal ions and the ligand(s)-to-metal charge transfer is uncovered. The latter property not only explicates the Irving-Williams series but also rationalizes quantitatively the Pearson's concept of hard and soft acids and bases by correlating the gas-phase to the aqueous-solution-phase chemistry in a broad sense.

Several decades passed away since Werner-type acceptor-donor acid-base complexes of the transition metal ions have been discovered. [1] The complex forming capacities of these ions with varieties of ligand systems is generally characterized with their stability constants, symbolically represented by log β (also known as equilibrium/formation/binding constant). In the +2 oxidation state the high-spin late first-row transition series metal ions commonly display a unique sequence in the experimental log β values, Mn < Fe < Co < Ni < Cu > Zn.[2] To give an example, the experimental log β values reported for the ethylenediiminodiacetate complexes of the six metal ions following the above sequence are ca. 7.0 (Mn^{2+}), 8.63 (Fe^{2+}), 11.25 (Co^{2+}), 13.6 (Ni^{2+}), 16.2 (Cu^{2+}), and 11.1 (Zn^{2+}), respectively (all measured at 25 °C with an ionic strength μ of 0.1, expect for the Zn^{2+} complex which was measured at 30 °C).[3-4] This above sequence initially put forwarded in 1948 was confirmed later in 1953, [2b] and is the so-called Irving-Williams thermodynamic series. Since then the series has become the subject of thousands of research articles because it refers to the relative stabilities of complexes formed by the late transition series metal ions, no matter which type of ligand coordinates to these ions, and because it adequately help rationalize the Pearson's fundamental concept of hard and soft acids and bases (HSAB).[5] Not only this, but it also serves guide designing novel ligand systems excellent for chelating, complexing affinity, and metal ion selectivity. [6] Recently, some of us, [7a-e] and several others, [8] have argued that the sequence may be an outcome of the interplay between covalent and ionic contributions to the metal-ligand binding energies, in reasonable agreement with a suggestion of Irving and Williams, [2b] but in somewhat odd with the crystal field theory that assumes the coordination between the metal core and the ligand(s) in a complex is purely electrostatic.

An accurate determination of (stepwise) stability constant(s) of complexation reactions (e.g., $[M(H_2O)_6]^{2+} + nL \leftrightharpoons [M(L)_n(H_2O)_{6-n}]^{2+}$, where n = 1–6 and L = ligand) in aqueous solution remains a formidable challenge both theoretically and experimentally to quantify chemical equilibria. The NMR spectroscopy, [9] the Electrospray mass spectrometry, [10] the van't Hoff plots, [11] and the pH-metric[12] methods are the recurrent experimental techniques that are vastly used for the determination of unknown log β values for a variety of metal complexes in aqueous solution. However, there are unavoidable circumstances that may arise because of hydrolysis for which indirect measurements with inaccurate log β values have also been suggested for many complexes of the M^{2+} ions. [4, 6a, 13] For ligands with saturated donors, (e.g., NH_3 (Fig. 1a) EDA (Fig. 1b), DETA (Fig. 1c), and TETRAEN (Fig. 1h), etc), the metal ions are normally being more acidic, one has superficially any difficulty in measuring the log β values. However, for ligands with unsaturated donors, the experimental situation becomes more complicated and the log β values reported often possess large experimental uncertainties. In any case, an understanding of the relative difference between the stability constants of the transition metal ion complexes containing saturated and unsaturated donors is of prodigious experimental and computational importance not only for designing novel ligand

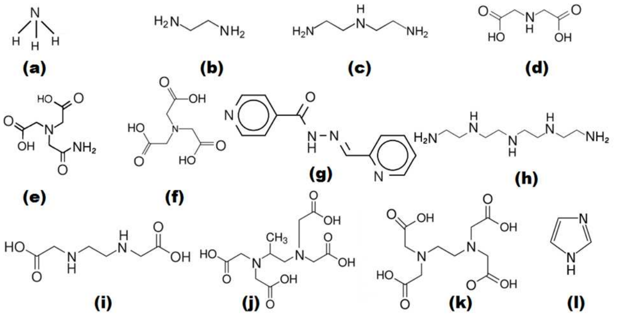

Fig. 1: Skeletal representations of the non-chelating/ chelating ligands considered. These include: (a) ammonia (NH_3), (b) ethylenediamine (EDA, $C_2H_8N_2$), (c) diethylenetriamine (DETA, $C_4H_{13}N_3$), (d) iminodiacetic acid (H_2IDA, $C_4H_7NO_4$), (e) ethylenediamine-N,N-diacetic acid (N-(2-aminoehtyl)iminodiacetic acid) (H_2AEIDA, $C_6H_{12}N_2O_4$), (f) 2,2′,2′′-nitriloacetic acid (H_3NTA, $C_6H_9NO_6$), (g) 2-pyridinecarbaldehyde isonicotinoylhydrazone (HPCIH, $C_{12}H_{10}N_3O$), (h) 1,4,7,10,13-pentaazatridecane (tetraethylenepentamine) (TETRAEN, $C_8H_{23}N_5$), (i) ethylenediiminodiacetic acid (H_2EDDA, $C_6H_{12}N_2O_4$), (j) propylene-1, 2-diaminotetra-acetic acid (H_4PDTA, $C_{11}H_{18}N_2O_8$), (k) ethylenedinitrilotetraacetic acid (H_4EDTA, $C_{10}H_{16}N_2O_8$), and (l) imidazole ($C_3H_4N_2$).

systems, but also for assessing the Lewis acid and the Lewis base behaviour in aqueous solution.

Moreover, numerous debates in the literature concern about factors that control the stability constants of diverse metal ion complexes in aqueous solution. [7,14] Yet none of the factors (e.g. electronegativity, entropy, charge of the electron donor complexing agents, and effective ionic radii of metal ions, etc), regarded as *standalone*. In order to provide some insightful description to the innovative chemistry of metal-ligand interactions, Hancock and Bartolotti[6a] have attempted mapping experimentally estimated aqueous solution phase and Density Functional Theory (DFT) calculated gas-phase free energies ΔG^o for a number of metal complexes in their +2 and +3 oxidation states. They have concluded in that study that DFT is an efficient tool for predicting unknown aqueous solution phase stability constants of metal ions with unidentate ligands (e.g., NH_3).

In this prospective article, we are interested in particular ligand(s)-to-metal charge transfer, an inherently occurred stabilizing force between the metal ion and the ligand(s) surrounding it, to elucidate whether this could offer a fundamental physical basis discerning the Irving-Williams series for the late first-row bivalent metal ions.[2] The term ligand(s)-metal charge transfer we consider is somehow homologous to the term 'inter- and intra-molecular electron transfer', a property which has been referred in the past to understand the noncovalent chemistry of hydrogen- and halogen-bonded complexes. According to Scholfield et al,[15] complexes involving these latter interactions, which were called as 'charge transfer bonds' are referring to a bonding model in which the charge from the lone pairs of an electron-rich atom, such as an oxygen or nitrogen, is transferred to a Lewis acid in a manner similar to what is commonly observed with transition metal complexes.[7] Legon and co-workers, [16] in many occasions, have determined the fraction of an electronic charge (typically $< 0.05\ e$) that is transferred from the Lewis base B to atom X of the XY molecule from the changes in the X and Y nuclear quadrupole coupling constants accompanying formation of the B···XY halogen bonded complexes. They have correlated this property with the first ionization potential of a number of Lewis bases, and with the bond force constants, and have demonstrated this as a measure of the strength of an interaction. Similarly, giving an IUPAC definition to hydrogen bond, Arunan et al have stated that this sort of charge transfer within a Lewis-acid and -base pair might lead to partial covalent bond formation.[17]

The approach we are adopting here for the fundamental understanding of the Irving-Williams series differs from many previous attempts in a sense that it does not involve the free energy and entropic calculations, which are commonly evaluated for elucidating chemical reactions at equilibrium. [6] These latter calculations are computationally much more demanding because an evaluation of these does not only rely on the energy-minimized geometries and the zero-point vibrational effects accompanied with both the monomers and complexes involved, but also overly sensitive to the level of electron-electron correlation and the nature of basis sets employed. Over and above, it has been recognized that the formation of a stronger metal-ligand complex accompanies a large negative value of ΔG^o, which is not so for metal complexes with weak donor ligands, as ΔG^o is negative and small for this latter case. And, there is no prior clue that clarifies, for instance, why we should expect stepwise stability constants log β_n (n = 1–6) for the ML_n complexes (viz. $[M(NH_3)_n(H_2O)_{6-n}]^{2+}$) to decrease in magnitude as n, the number of ligands (e.g., NH_3), increase in aqueous solution, where M = Mn, Fe, and so forth. [3-4] Thus to deepen our fundamental understanding into all these above issues, we use theoretical approaches to assess the fractional electronic charges, but not the energies associated with these, [18] that are to be transferred largely from the nonbonding electron-rich orbitals of the ligand donors to the unfilled valence accepting orbitals of the transition metal ions, thereby promoting formation of the coordination complexes. In order to do so, we estimate the extent of electric charge redistribution, compared to the isolated subunits, that accompanies metal complex formation. Note that atomic charges are quantum expectation values determined by quantum mechanics, and these and their changes, with vibrational motion for example, are in many cases measurable.[19]

We performed DFT-based spin-restricted (for Zn^{2+}) and -unrestricted (for all the other five divalent ions) electronic structure calculations for a total of 78 metal complexes in the gas phase, which are composed of neutral, cationic, and anionic species. Fig. 1 illustrates all the twelve ligands considered, which are the vastly (experimentally) studied industrially important biologically relevant topologically different neutral and protonated ligands. For reasons adequately described elsewhere, [20] the PBE1PBE functional (in short, PBE0), [21] together with the 6–311++G(d,p) basis set, ultrafine integration grid and self-consistent-field convergence (fermi) criteria instead of default settings, was employed for geometry minimizations and Hessian calculations. The high-spin states of the metal ions involved were 6, 5, 4, 3, 2, and 1 for Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+}, respectively. The solid state geometries of many of these transition metal complexes considered were obtained from the Cambridge Structural Database.[22] These geometries each was energy-minimized to be a stationary point on the respective potential energy hyper-surface, confirmed by Hessian calculations. The coordination geometry around the metal ion in most of the energy-minimized geometries of the complexes is turn out to be a pseudo octahedron, similar to what was found in the solid state. Fig. 2 shows the coordination geometries of some of the randomly

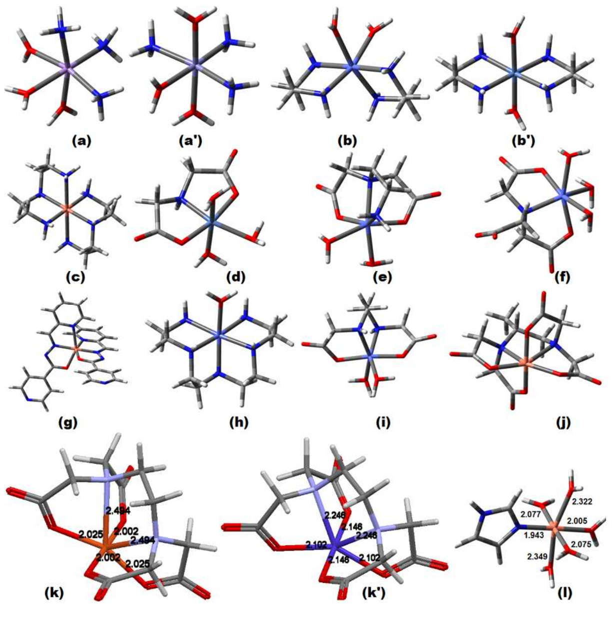

Fig. 2: Tube models of some selected energy-minimized geometries of the transition metal complexes obtained using PBE0/6-311++G(d,p). These include: fac-$[Co(NH_3)(H_2O)_2]^{2+}$ (a), mer-$[Co(NH_3)(H_2O)_2]^{2+}$ (a'), cis-$[Co(EDA)_2(H_2O)_2]^{2+}$ (b), trans-$[Co(EDA)_2(H_2O)_2]^{2+}$ (b'), $[Cu(DETA)_2(H_2O)_2]^{2+}$ (c), $[Cu(IDA)(H_2O)_3]$ (d), $[Co(AEIDA)(H_2O)_2]$ (e), $[Co(NTA)(H_2O)_3]^{-1}$ (f), $[Cu(PCIH)_2]$ (g), $[Co(TETRAEN)(H_2O)]^{2+}$ (h), $[Co(EDDA)(H_2O)_2]$ (i), $[Cu(PDTA)]^{2-}$ (j), $[Cu(EDTA)]^{2-}$(k), $[Co(EDTA)]^{2-}$ (k'), and $[Cu(imidazole)(H_2O)_5]^{2+}$ (l). The metal-ligand bond distances depicted in (k), and (k') display equatorially distorted geometries of the Cu^{2+} and Co^{2+} ions, while that depicted in (l) displays axially distorted geometry of the Cu^{2+} ion, both caused by the Jahn-Teller effect.

selected complexes involving the Co^{2+} and Cu^{2+} ions that include at least one complex from each series constituting a given type of ligand. In several cases, the $3d^9$ Cu^{2+} ion complexes are having two pairs of four nearly equivalent metal-ligand bonds and the other two are elongated along the axial (or equatorial) direction, a consequence of Jahn-Teller distortion. For the $3d^7$ Co^{2+} ion complexes, on the other hand, the Jahn-Teller distortion is found to be much less severe, as expected. [7a-b,d] Figs. 2k and 2k' explain the feature for the Co^{2+} and Cu^{2+} complexes of the $EDTA^{4-}$ ligand, respectively.

An application of Quantum Theory of Atoms in Molecules (QTAIM), [23] a detail of which is already catalogued elsewhere, [23-24] to the equilibrium geometries of the transition metal complexes obtained from the DFT calculations gave topological electron density properties and integrated QTAIM charges. The latter are conferred on atoms that constitute the metal complexes. The QTAIM ligand(s)-to-metal charge transfer, quantified by ΔQ, is calculated by subtracting the net electronic charge conferred on the metal ion in each of these 78 complexes from that of the formal +2 charge of the free ion. For some of the metal complexes with geometrical isomers, an average QTAIM charge was estimated for each pair (e.g., fac and mer isomers of $[M(H_2O)_3(NH_3)_3]^{2+}$ (Figs. 2a and 2a'), and cis and trans isomers of $[M(EDA)_2(H_2O)_2]^{2+}$ (Figs. 2b and 2b'), etc) to calculate ΔQ. To provide insight into the orbital populations of the most important bonding, nonbonding, and valence accepting orbitals involved, Natural Population Analysis (NPA) [25] was performed with the same level of theory on the optimized DFT geometries of the complexes. All the electronic structure calculations were performed using GAUSSIAN 09[26] and AIMALL[27] suites of programs.

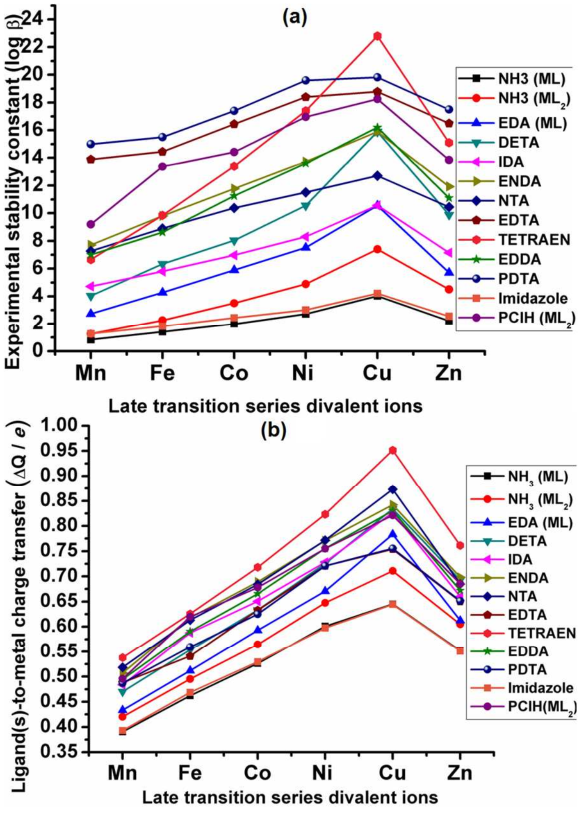

Fig. 3: Dependence of experimentally measured stability constants log β (a), and DFT calculated ligand(s)-to-metal charge transfer ΔQ (b), on the atomic number of the late first-row transition series divalent metal ions for a variety of complexes. Both the graphs (a) and (b) reveal the famous Irving-Williams series. Experimental log β values reported with the μ value of 0.0/0.1/1.0 at 20/25/30 °C were obtained from the NIST database.[3] Refer Fig. 1 regarding the details of the ligands considered.

QTAIM ligand(s)-to-metal charge transfer values for the whole series of 78 metal-ligand complexes investigated are estimated to lie between 0.391 and 0.951 *e*, a range which is between 35 and 95% of an electron, a range that is indeed much larger than that expected upon the formation of hydrogen- and halogen-bonded complexes (values typically much less than an order of a few tenths of an electronic charge). The abovementioned values are the minimum and maximum of ΔQ that are associated with the $[Mn(H_2O)_5(NH_3)_1]^{2+}$ and $[Cu(H_2O)(TETRAEN)]^{2+}$ complexes, respectively, in excellent agreement with the experimental log β values of 0.84 and 22.8 for the corresponding complexes, respectively, reported at 25 °C with μ = 0.0. [3-4] NPA stipulates such a large ΔQ is due to the population of the triply degenerate t_{2g} (d_{xy}, d_{yz}, d_{zx}) and doubly degenerate e_g (d_{z^2}, $d_{x^2-y^2}$) orbitals of the 3d ions caused by the partial transferred charges from the O and/or N occupied nonbonding electron orbitals of the ligand donors. Note that ΔQ is not only entirely due to the electron occupation of the 3d orbitals of the ions, but also in part due to the fractional electrons occupied of the $4s^0$ valence accepting orbital of the ions. This latter orbital is occupied with roughly 0.16 – 0.36 electrons for the whole series of complexes examined. An occupancy of this orbital is in consistent with the fact that the energy difference between the *md* and (*m* + *1*)*s* orbitals for the M^{2+} ions is very marginal for which not all electrons from the ligand's Lewis base centres transferred the *md* orbital of the metal ion, but rather a fraction of them are squeezed into the $(m + 1)s^0$ orbital of it.[7a,28] These results suggest that the first-row transition series divalent ions may not necessarily be constricted to possess a $3d^m4s^0$ (n = 1−10) electronic arrangement especially when they are bonded to the electron-rich donors.

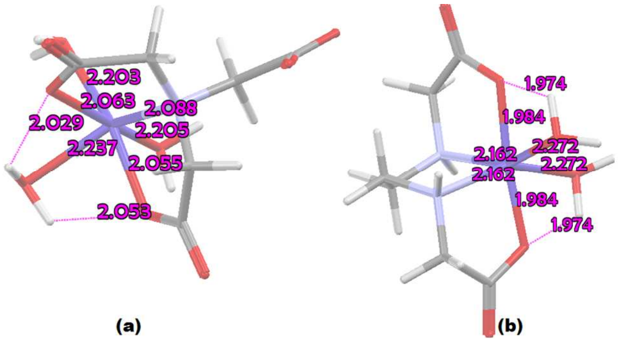

Fig. 4: Examples illustrating the $[Co(NTA)(H_2O)_3]^{-1}$ (a), and $[Co(EDDA)(H_2O)_3]$ (b) complexes involving the O···H (hydrogen-bonded) inter-ligand interactions (dotted lines). The metal-ligand coordinate bonds are also depicted to infer the extent of geometrical asymmetry around the metal ion, caused by the Jahn-Teller effect.

Given a ligand, ΔQ is found to be the least for the complex with the Mn^{2+} ion, increases steadily increasing the atomic number of the metal ions across the series (as the metal becomes more acidic), becomes a maximum for the complex with the Cu^{2+} ion, and then decreases for Zn^{2+}. This specific is sharply in consistent with the trend previously observed for the experimental log β values of the corresponding complexes. For instance, the reported log β values for the deprotonated complexes of AEIDA with Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+} are ca. 7.71, 9.81, 11.78, 13.73, 15.90, and 11.93, respectively, measured at 20 °C with a μ value of 0.1 and K+ as a background electrolyte.[3-4] This trend in log β is perfectly in line with the calculated ΔQ, which are ca. 0.508, 0.618, 0.689, 0.771, 0.842, and 0.698 e for the corresponding complexes, respectively. Similarly, the log β (ΔQ/e) values for the IDA complexes of these metal ions are ca. 4.72 (0.483), 5.80 (0.588), 6.97 (0.651), 8.30

(0.728), 10.56 (0.827), and 7.15 (0.660), respectively, with the log β values reported at 25 ^{o}C with μ = 0.1.[3-4] For the most stable $[M(TETRAEN)(H_2O)]^{2+}$ complexes in the whole series, the log β (ΔQ/e) values are ca. 6.55 (0.538), 9.85 (0.626), 13.40 (0.718), 17.40 (0.823), 22.80 (0.951), and 15.10 (0.761), respectively, with the log β values reported at 25 ^{o}C with μ = 0.1.[3-4] As can immediately be seen from these data, the most stable complex formed of each ligand in each series is associated with the Cu^{2+} ion. This is not unexpected as the coordination between the metal core and the donors leads to partial covalent bond formation, the extent of which is being the largest for the Cu^{2+} complexes, which is likely due to the four metal-ligand contacts which are remarkably shorter (values in the 1.8–2.1 Å range) compared to the other two axial/equatorial bonds (values in the 2.4 – 2.6 Å range) (see Figs. 2k and 2l for more detail).

Figs. 3a and 3b illustrates the plots of log β and ΔQ values against the atomic number for a variety of complexes of the late metal ions, respectively. Each coloured line in these plots represents to a given type of ligand, and each of them represents the Irving-Williams series,[2] $Mn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} > Zn^{2+}$. This reveals the series is reminiscent of any ligand, again this no matter whether it is mono-, or bi-, or poly-dentate, and whether the ligators are purely O, N, or mixed type (*cf.* Fig. 1). The somewhat irregular overlapping between the coloured lines in these graphs is a result of the scattered ΔQ and log β values, which are associated with most of the acetate containing ligand complexes of the metal ions. We attribute the irregularity in ΔQ to the secondary interactions involved. These interactions are inherently present within the first coordination sphere of the metal ions in the form of ligand strain, or back bonding interaction (which are due to partial release of electrons from the 3d orbitals of the metal ions to the π* anti-bonding orbitals of the –C=O bonds), or prolonged hydrogen-bonded interactions between the ligands (inter-ligand). Fig. 4 shows, for examples, the latter feature comprising of the O···H hydrogen-bonded interactions.

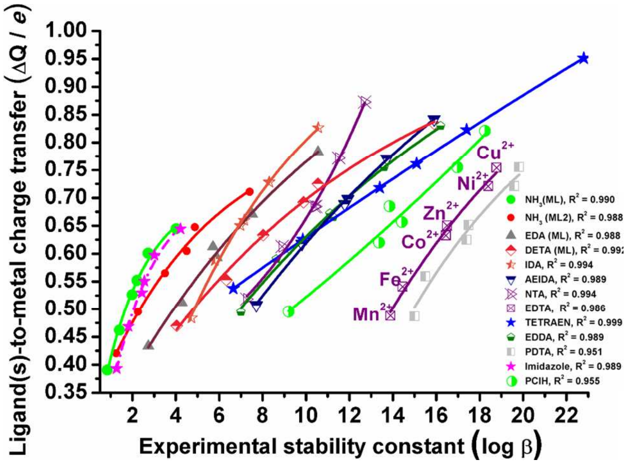

Fig. 5: Relationship between experimental aqueous solution phase stability constants log β and DFT calculated gas-phase ligands-to-metal charge transfer ΔQ for a variety of ligand complexes of the late transition series first-row M^{2+} ions. Individual regression line in the plot represents the data of a given ligand type, and is the result of fitting the data to a first order exponential function of the form $\Delta Q = \Delta Q_o + A \exp(-\log \beta/t)$, wherein ΔQ_o, A and t are the offset, amplitude and decay constant, respectively. The lines indicate variable slopes and intercepts (all other than unity), which are not unexpected as solvation contributes in part to the log β_n. An adjusted regression coefficient (R^2) is shown for each case. Experimental log β values reported with the μ value of 0.0/0.1/1.0 at 20/25/30 ^{o}C were obtained from the NIST database.[3] Refer Fig. 1 regarding the details of the ligands considered.

Fig. 5 illustrates the unified plot of experimental log β vs. calculated ΔQ for the 78 mononuclear complexes of the late transition series metal ions (for the ammonia ligand, both the ML_1 and ML_2 complexes are included). As can be evidently seen from the graph, not all the 78 data points fit to a given mathematical function, suggesting that each ligand has its own characteristic property (e.g., affinity for binding and selectivity, etc) towards the six metal ions uncommon with that of the other ligands examined. However, each data set corresponding to a given ligand is fitted, whilst not very perfect, to a first order exponential function of the form $\Delta Q = \Delta Q_o + A \exp(-\log \beta/t)$, where ΔQ_o, A and t are the offset, amplitude and decay constant, respectively. Each fitted line possesses an appreciable regression coefficient R^2, values ranging between 0.98 and 0.99 for all lines. The slope and intercept of each regression line differ from that of the other, thereby likely discriminating theory from experiments, reflecting the fact that the latter performed with different conditions of temperature, pressure, background electrolyte and solvent, etc. Moreover, the slope for none of the curves is unity, meaning that the effect of solvation not considered here might be playing some minor role in the stabilization of the complexes. Incontrovertibly, the correlations in Fig. 5 stipulate that ΔQ is indeed a factor vividly responsible for the stabilization of the metal-ligand coordinate bonds in the metal complexes investigated. Moreover, the graphs in both Figs. 3 and 5 suggest that one may regard ΔQ as an alternative to elucidate the relative stability constants of the metal ions in aqueous solution, and that the Irving-Williams series being a consequence of stabilizing ΔQ that promotes the metal's Lewis acid center to coordinate with Ligand's Lewis base center at the equilibrium geometry of the transition metal complexes.

Next, we aim at addressing whether we can use ΔQ as a predicting tool for the determination of unknown stepwise stability constants of the transition metal complexes. To enlighten this, let us consider, for example, the six-coordinate aqua-ammine complexes of the M^{2+}ions, $[M(NH_3)_n(H_2O)_{6-n}]^{2+}$, where (M = Mn, Fe, ..., Zn) and n = 0–6. The experimental log β_n values for several of these metal complexes have been reported in aqueous solution. However, there is no reasonable readymade data available for log β_n for some of these complexes because at higher pH the loss of ammonia is abruptly enhanced in water. What are feasible are experimentally either unknown or values of the log β_n with large experimental uncertainties. For instance, a NIST critically selected stability constant database[19-20] survey gave a value of 1.24 for log β_4 for the ML_4 complex of $[Mn(NH_3)_m(H_2O)_{6-m}]^{2+}$, a value which is unexpectedly smaller than the log β_3 value of 1.38 for the corresponding ML_3 complex, both determined at 25 ^{o}C. There are no data reported for log β_4 and log β_5 for the corresponding ML_5 and ML_6 complexes of the Mn^{2+} ion. Similarly, for the Ni^{2+} ion, log β_6 for the ML_6 complex is reported to be unusually smaller than log β_5 for the corresponding ML_5 complex (8.30 vs. 8.33). In the same way, there are no log β data available for the ML_4 and ML_5 complexes of the Fe^{2+} ion, as well as that for the ML_6 complex of the Co^{2+} ion. Nevertheless, we plotted log β_n against ΔQ in Fig. 6a for the six-coordinate aqua-ammine complexes of the Fe^{2+}, Co^{2+} and Ni^{2+} ions. The data for each metal ion are fitted to a first order exponential function, similar to the ones described in Fig. 5, but for this case, log β_6 for the ML_6 complex of the Ni^{2+} ion (see the black line), and log β_5 for the ML_5 complex of the Co^{2+} ion (see the red line) are an outlier. The regression analyses helped predict values of 5.43 and 5.58 for log β_5 and log β_6 for the ML_5 and ML_6 complexes of the Co^{2+} ion, respectively, and a value of 8.99 for log β_6 for the ML_6 complex of the Ni^{2+} ion. As expected, the latter value for the ML_6 complex of the Ni^{2+} ion is about 0.69 log units larger than the corresponding value of 8.30 reported experimentally. Similarly, for the ML_5 and ML_6 complexes of the Fe^{2+} ion, values of 2.96 and 3.01 are predicted for log β_5 and log β_6, respectively.

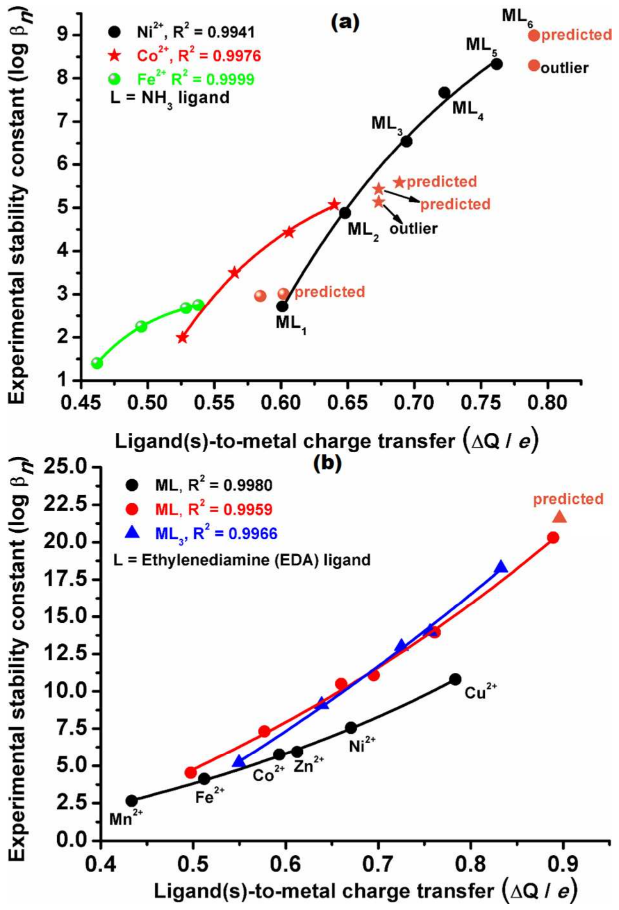

Fig. 6: (a) Experimental stability constants log β_n are plotted as a function of the DFT calculated ligand(s)-to-metal charge transfer ΔQ for the six-coordinate $[M(NH_3)_n(H_2O)_{6-n}]^{2+}$ complexes; experimental log β_n values reported with the μ value of 0.0/0.1/1.0 at 20/25/30 °C were obtained from the NIST database.[3]A similar dependence is given in (b) for the ML,ML_2, and ML_3 aqua-ethylenediamine complexes of the six metal ions (experimental log β_n values estimated with the μ value of 1.0 at 25 °C were obtained from the NIST database[3]). In each plot, the data for individual complex type are fitted to a first order exponential function of the form log $\beta_n = \Delta Q_o + A\ e^{(-\Delta Q/t)}$, wherein ΔQ_o, A and t are the offset, amplitude and decay constant, respectively. The log β_n values which do not fit to the above function are shown as 'outliers' in both the plots, and the ones which are marked as 'predicted' in orange are estimated using the parameters obtained from the respective regression analysis.

Illustrated in Fig. 6b are plots of experimental log β_n vs. calculated ΔQ for the ML, ML_2, and ML_3 EDA (ethylediamine) complexes of the six metal ions. In each case, the data are excellently fitted to a first order exponential function. And, using the regression parameters, the unknown stability constant log β_3 for the $[Cu(EDA)_3]^{2+}$ complex is estimated to be 21.60.

In summary, the methodology we employed here has not only allowed us establishing a novel connection between the gas phase ΔQ and the aqueous solution phase log β in a broad sense, but also provided us with some confidence on the reliability of the integrated QTAIM charges. The correlation we sought enabled us realizing ligand(s)-to-metal charge transfer as a factor governing the origin of the Irving-Williams series. It also offers us the privilege to regard this physically meaningful quantity to help predict the aqueous solution phase stepwise stability constants of the M^{2+} ions with unidentate ligands and beyond. We are presently exploring the log β vs. ΔQ relationship in several other metal complexes constituting ligands of varied types, and we report our results elsewhere.

Notes and references

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Graphical abstract: