A Glance at the Stabilities of Transition Metal Complexes with Ligands Having N and O Donor Atoms

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ABSTRACT: The stability of metal complex generally means that it exists under favorable conditions without undergoing decomposition and has a considerable shelf life period [1]. The term stability of metal complex cannot be generalized since the complex may be stable to one reagent/condition and may decompose in presence of another reagent/condition. The stability of metal complexes can be explained with the help of two different aspects, namely, thermodynamic stability and kinetic stability [2]. Nevertheless, a metal complex is said to be stable if it does not react with water, which would lead to a decrease in the free energy of the system, i.e., thermodynamic stability. On the other hand, the complex is said to possess kinetic stability if it reacts with water to form a stable product and there is a known mechanism through which the reaction can proceed. For example, the system may not have sufficient energy available to break a strong bond, although once the existing bond is broken it could be replaced by new bond which is stronger than the older one [1]. Stability of complex compound is assigned to be its existence in aqueous solution with respect to its bond dissociation energy, Gibbs free energy, standard electrode potential, pH of the solution, and rate constant or activation energy for substitution reactions.

KEYWORDS-stability,metal,complexes,transition,ligands,donor,atoms

I. INTRODUCTION

N donor ligands for tetravalent Co must be carefully designed in order to prevent disproportionation (ligand dehydrogenation/Co reduction). A key feature is that no H atoms must be present on the C atoms adjacent to the coordinated N-donor. A range of multidentate amide ligands capable of stabilizing high oxidation states of Co have been reported.[1,2] The Co^{IV} complex (250) (X = 4-t-Bu-pyridine) of the dioxo-salphn analog was prepared by Ce^{IV} oxidation of the trivalent analog. The presence of four ionizable donor atoms enables the ligand to stabilize this high formal oxidation state and the compound was characterized structurally.[1105] The frozen solution EPR spectrum (10 K) of the complex exhibits an eight-line pattern from hyperfine coupling (16 G) of the single unpaired electron to the Co nucleus (I = 7/2), centered at g = 2.011. The emergence of three visible maxima in the spectrum of this complex not seen in the precursor was also indicative of metal-centered oxidation. Two sequential reversible electrochemical oxidations of the Co^{III} complex were observed 0.39 V and 0.84 V more positive than the Fc/Fc$^+$ reference. The square–planar tetravalent complex (251) has been reported along with its 4,5-dihalobenzo analogs.[1106] EPR data in toluene at 5.9 K are consistent with a single unpaired electron residing on the metal center. The complex slowly oxidizes H_2O, yielding the trivalent complex. Replacement of the gem dimethyl groups of (251) with spiro-cyclohexyl moieties and attachment of methoxyl aromatic substituents results in an effective one-electron oxidant in cyclohexane solutions. A number of charge transfer salts of this tetravalent complex with single electron reductants such as ferrocene, N,N′-tetramethyl-p-phenylenediamine and Mg(TPP) were isolated.[1107] Reaction with PhSH gave PhSSPh and with Bu$_3$SnH gave the tributyltin dimer, while the reduced trivalent monoanionic complex precipitates quantitatively following reaction.[3,5]

(250)   (251)
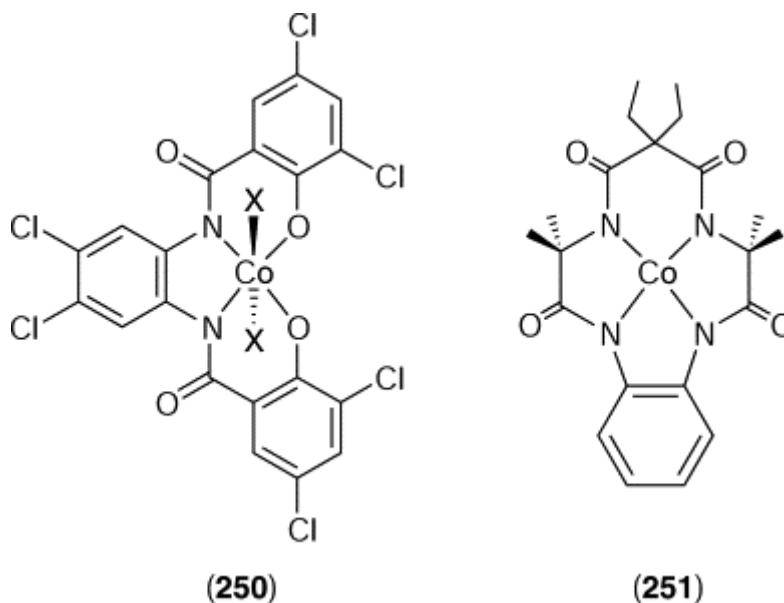
II. DISCUSSION

Neutral N-donor ligands have been used to stabilize novel subhalide clusters of Ga and In. Schnöckel and co-workers obtained triethylamine-stabilized octameric aggregate $Ga_8Br_8(NEt_3)_6$ as well as the tetrameric compounds $Ga_4Br_4L_4$ (L = NEt_3, py, NH_3) from metastable monovalent gallium(I)bromide solutions.[134] Dissolution of indium(I)iodide in TMEDA afforded the moderately stable cluster complex $In_6I_8(TMEDA)_4$, which allowed insights into the structures of low-oxidation state In halides in donor-solvent solutions.[135] In contrast to Al(I) and Ga(I) halides, disproportionation reactions of In(I) halides were investigated to a far lesser extent.[7,8]

Moreover, pyridine-based ligands have been coordinated to M(I) (M = In, Tl) cations. Aldridge and co-workers employed a 2,6-diarylpyridine ligand, the neutral counterpart to Power's anionic terphenyl ligands, to isolate the formally analogous cationic indane- and thallanediyls, $[(2,6-Mes_2C_5H_3N)M(solv)_n][B(3,5-(CF_3)_2C_6H_3)_4]$ (M = In, solv = C_6H_5F, n = 1 (126); M = Tl, solv = C_6H_5F, n = 2 (127); M = Tl, solv = tol, n = 2 (128)), which were found to exhibit weak interactions with solvent molecules in the solid-state. The two-coordinate dipyridine In complex $[(2,6-Mes_2C_5H_5N)_2In][B(3,5-(CF_3)_2C_6H_3)_4]$ (129) was also obtained.[136] Richeson and co-workers used bis(imino)pyridine ligands for the stabilization of low-coordinate In(I) and Tl(I) cations including $[[{ArNCPh}_2(NC_5H_3)]M][OSO_2CF_3]$ (M = In, Tl; Ar = 2,5-$tBu_2C_6H_3$, Dip, 2,6-$Et_2C_6H_3$) and $[{[{ArNCPh}_2(NC_5H_3)]Tl}_2(\mu-solv)][OSO_2CF_3]$ (solv = C_6H_6, tol). Structural findings such as the long M–N bonds in these pyridine complexes in combination with results from DFT calculations indicated only weak orbital/covalent interactions due to a discrepancy of the donor and acceptor orbital energies, while noncovalent interactions were determined to be important, particularly in the Tl complexes.[137–139]

Krossing and co-workers employed aromatic N-bases, 2,6-tBu-4-MeC_5H_2N and pyrazine, as ligands for Ga^+ cations, which feature the option for σ and π coordination, and found that the σ coordination via the nitrogen lone pairs is preferred.[140] Moreover, they isolated polycationic cluster-type complexes of donor-stabilized M(I) cations (M = Ga, In) of the type $[M_nL_m]^{n+}$, which were formed upon addition of donor solvents such as 2,2′-bipyridine (bipy), 1,10-phenanthroline (phen), $tBuNC$, and DMAP, to solutions of $[M(C_6H_5F)_2][Al(OC(CF_3)_3)_4]$. In case of indium, different triangular clusters such as $[In_3(bipy)_6]^{3+}$ (130), $[In_3(bipy)_5]^{3+}$ (131) as well as rhombic clusters, i.e. $[In_4(bipy)_6]^{4+}$ (132), $[In_4(phen)_6]^{4+}$ (133), were isolated, depending on the reaction conditions. The strongly-coordinating bipy ligand was used for the stabilization of the monometallic paramagnetic dication $[Ga(bipy)_3]^{2+}$ (134) containing a Ga(III) center, which was formed via disproportionation reaction of the starting low-valent gallium species. Dication 134 was disclosed as a ligand-centered radical by EPR spectroscopy.[141] Disproportionation reactions also occurred upon treatment of Ga(I) with the phen ligand, resulting in the formation of the dimeric Ga–Ga bonded Ga(II) tetracation $[Ga_2(phen)_4]^{4+}$ (135). Reaction of 135 with isocyanide $tBuNC$ yielded the tetracation $[Ga_4(tBuNC)_8]^{4+}$ (136) containing a square-planar Ga_4 ring,[142] whereas the analogous reaction with DMAP gave the pentagonal-planar pentacation $[Ga_5(DMAP)_{10}]^{5+}$ (137), respectively.[143] According to quantum chemical calculations, the cluster formation proceeds stepwise via the triplet state fragments, while the driving force for the formation of these unusual aggregates was assumed to rely on the strong M–M bonds and the high lattice energy of the salts, which outperform the Coulombic repulsion[141–143] [9,10]
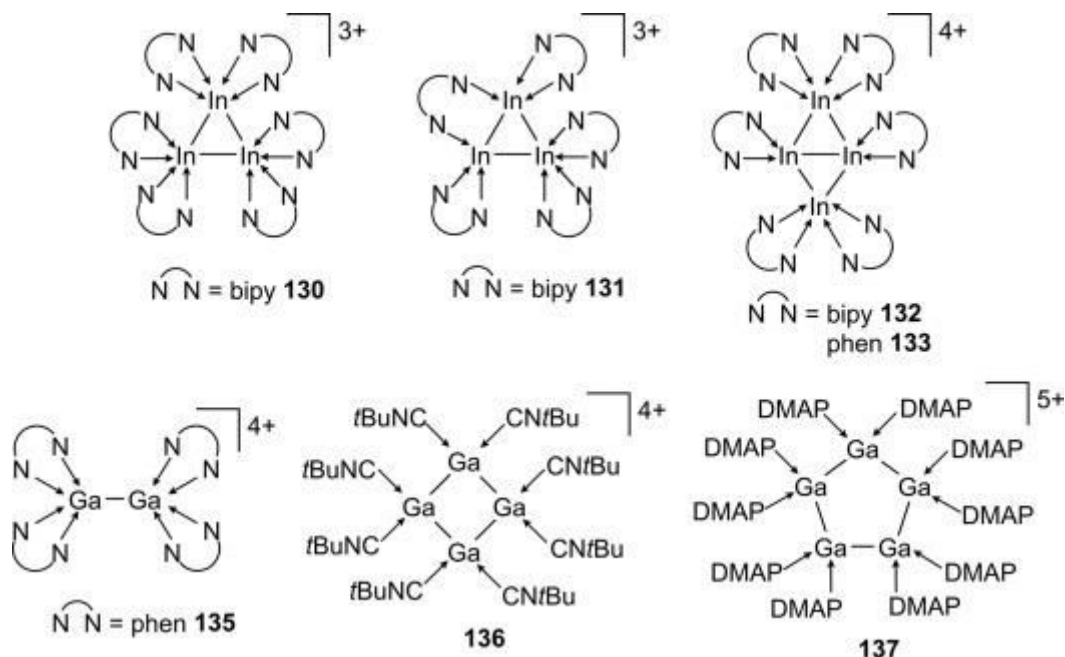
III. RESULTS

The Irving-Williams Series refers to the relative stabilities of complexes formed by a metal ion. For high-spin complexes of the divalent ions of first-row transition metals, the stability constant for the formation of a complex follows the order: Mn(II) < Fe(II) < Co(II) < Ni(II) < Cu(II) > Zn(II) This order was found to hold for a wide variety of ligands The ionic radius is expected to decrease regularly for Mn2+ to Zn2+. This is the normal periodic trend and would account for the general increase in stability. The Crystal Field Stabilization Energy (CFSE) increases from zero for manganese(II) to a maximum at nickel(II).[11,12] This makes the complexes[19,20] increasingly stable. CFSE for zinc(II) is zero. Although the CFSE of copper(II) is less than that of nickel(II), octahedral copper(II) complexes are subject to the Jahn-Teller effect, which affords a complex extra stability. Crystal Field Theory is based on the idea that a purely electrostatic interaction exists between the central metal ion and the ligands. This suggests that the stability of the complexes should be related to the ionic potential; that is, the charge to radius ratio. In the Irving-Williams series, the trend is based on high-spin M(II) ions, so what needs to be considered is how the ionic radii vary across the d-block. For high-spin octahedral complexes it is essential to consider the effect of the removal of the degeneracy of the d-orbitals by the crystal field. Here the d-electrons will initially add to the lower t2g orbitals before filling the eg orbitals since for octahedral complexes, the t2g subset are directed in between the incoming ligands whilst the eg subset are directed towards the incoming ligands and cause maximum repulsion.[13,15] For the sequence Mn(II) to Zn(II), the crystal field (q/r) trend expected would be:

Mn(II) < Fe(II) < Co(II) < Ni(II) > Cu(II) > Zn(II) Apart from the position of Cu(II), this corresponds to the Irving-Williams series. The discrepancy is once again accounted for by the fact that copper(II) complexes are often distorted or not octahedral at all. When this is taken into consideration, it is seen that the Irving-Williams series can be explained quite well using Crystal Field Theory.[18,17]

IV. CONCLUSION

Pi bonding is not considered by crystal field theory, but is addressed in ligand field theory. The orbitals on the metal which were not used for sigma bonding (the t_{2g} set: d_{xy}, d_{yz}, d_{xz}) have the same symmetry properties as combinations of the p orbitals on the ligands. If the energy of the metal and ligand orbitals are comparable, the pi bonding orbitals formed will be significantly lower in energy thatn the atomic orbitals on either the metal or ligand. Likewise, the antibonding pi orbitals will be much higher in energy. If the orbitals are very different in energy, only slight mixing will occur. An example of pi overlap is shown below.
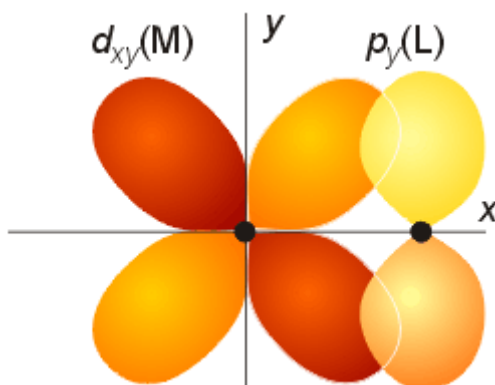
The effect on the molecular orbital diagram is as follows. The gap between the t_{2g} and e_g set will change, because the t_{2g} set is involved in bonding, so there is not a bonding t_{2g} set, and an antibonding t_{2g} set of orbitals. The gap, represented as D_o becomes the gap between the t_{2g} set of antibonding orbitals and the e_g set of orbitals. As a result, the size of D_o dimishes.[21,22]
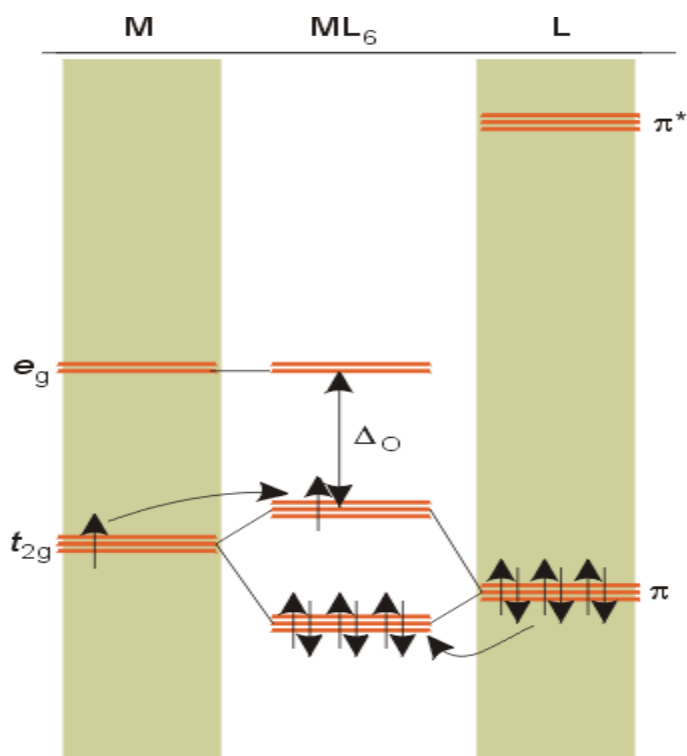
The above molecular orbital diagram is for ligands which have pi antibonding orbitals too high in energy to interact with the metal orbitals. The net effect for these pi donor ligands is to decrease the size of D_o compared to ligands which only act as sigma donors.

Ligands may have empty pi antibonding orbitals higher in energy and with the same symmetry as the t_{2g} orbitals of the metal. These ligands orbitals interact with the t_{2g} orbitals of the metal creating a bonding orbital which is slightly lower in energy than the t_{2g} set of the metal, and an antibonding set of orbitals which are much greater in energy than the e_g set of the complex. The net result is that the size of the splitting, D_o, increases, since the energy of the t_{2g} bonding orbitals drops a bit.[22,23]
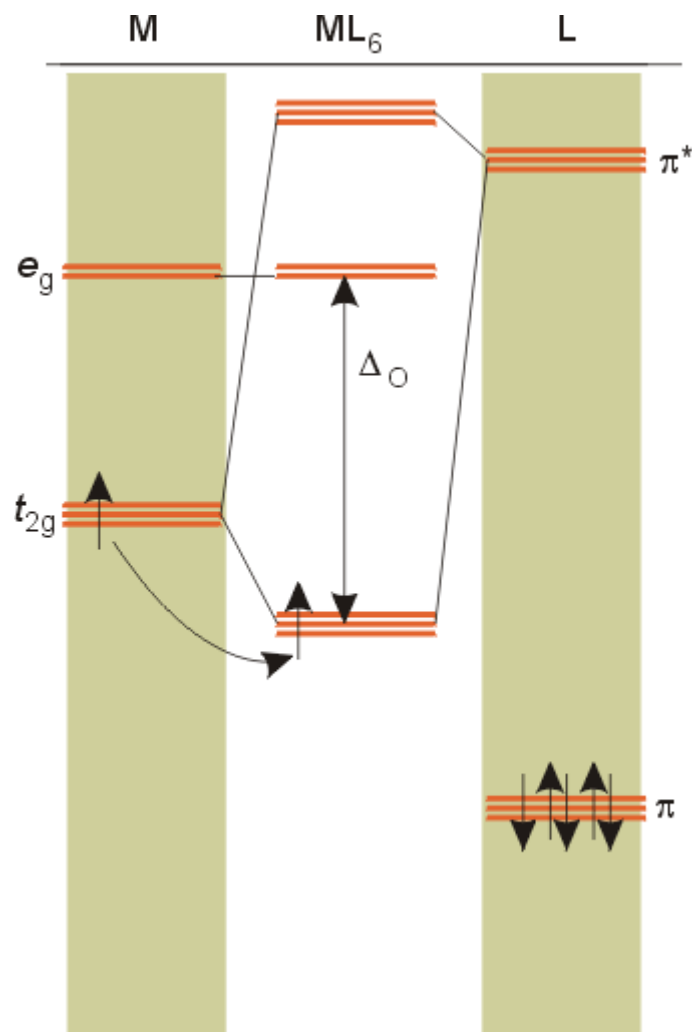
The net result is that pi acceptor ligands (such as CO and N_2), with empty antibonding orbitals available to accept electrons from the metal, increase the size of D_o. The spectrochemical series can be reconsidered with the possiblity of pi bonding in mind. It shows that the order (with some notable exceptions) goes as follows:

Strong p donor (small D_o) < weak p donor < no p effects (intermediate D_o)< p acceptor (large D_o)
The trend can be illustrated with the following ligands as examples:
$I^- < Br^- < Cl^- < F^- < H_2O < NH_3 < PR_3 < CO, CN^-$
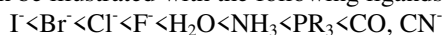
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