The Role of Inverted Ligand Field in the Electronic Structure and Reactivity of Octahedral Formal Platinum (IV) Complexes

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Abstract: Platinum complexes are ubiquitous in chemistry and largely used as catalysts or as precursors in drug chemistry, thus a deep knowledge of their electronic properties may help in planning new synthetic strategies or exploring new potential applications. Herein, the electronic structure of many octahedral platinum “IV” complexes is drastically revised especially when the metal is associated with electronegative elements such as halogens and chalcogens. The investigation revealed that in most of the cases the five d platinum orbitals are invariably full, thus the empty antibonding orbitals, usually localized on the metal, are mainly centered on the ligands, suggesting a questionable assignment of oxidation state IV. The analysis supports the occurrence of the Inverted Ligand Field theory in all cases with the only exceptions of the Pt-F and Pt-O bonding. The trends for the molecular complexes are mirrored also by the Density of States plots of extended structures featuring octahedral platinum moieties in association with chalcogens atoms. Based on the gathered information on the electronic structure of complexes and materials, the oxidative addition of a Se-Cl linkage to a square platinum complex to achieve an octahedral moiety has been revised in the framework of the Inverted Ligand Field.

Introduction

The classical accepted view of the metal-ligand interactions in a transition metal complex is based on the assumption that the ligand-based combinations are filled and at lower energy than the involved metal orbitals (Ligand Field Theory).[1-3] This description provides an immediate picture of the electronic distribution in most transition metal complexes. For the late transition metals, the energy of the d orbitals may be lower than the ligand ones. This has been reported for several square planar “d8” complexes where the b1g ligands combination lies in energy above the interacting metal dx2-y2 orbital.[4] As shown at the right side of Scheme 1, the resulting bonding orbital is mainly centered on
the metal while the antibonding one (usually the LUMO) features a stronger contribution from the ligands with an inversion of the electron population towards the metal center. This bonding picture in square planar complexes allowed the introduction of the concept of Inverted Ligand Field (ILF).\textsuperscript{[1,5]}

Scheme 1. Evolution of the electronic structure on increasing the energy of the $b_{1g}$ ligands’ combination for a square planar transition metal complex

The ILF theory, nowadays well supported by experimental data and calculations,\textsuperscript{[1,5-15]} provides a critical review of the high oxidation state in 11$^{th}$ group metals, suggesting that most of the d$^8$ Cu(III) and Au(III) square planar complexes could be better considered as d$^{10}$ Cu(I) and Au(I) ones. This new bond description allows a better knowledge of the reactivity of these systems, not always easily to be rationalized.

From Scheme 1, it is also evident that the LUMO becomes the key orbital for discriminating between a LF and a ILF descriptions. A metal contribution to the LUMO greater than 60% allows a more suitable description of the bonding within the classic LF theory with the bonding electrons more localized on the ligands. Otherwise, when the contribution of the metal to the LUMO is small (less than 40%) the ILF becomes operative, and the M-L bonding could be better described as covalent with the electrons more polarized toward the metal rather than the ligands. Obviously, a wide spectrum of intermediate situations of covalency is possible in the contribution range between 40 and 60% with the maximum of covalent bond for a 50% of percentage.\textsuperscript{[1,5,7]}

Herein, we explore the chance that ILF is active also in a coordination geometry alternative to the square planar, namely the octahedral one, and for platinum in oxidation state IV. In a classical viewpoint, the bonding in octahedral complexes could be described as six electron pairs donations from the six populated ligands into six empty suitable metal orbitals (one s, three ps and two ds in the $e_g$ set namely $d_{x^2-y^2}$ and $d_{z^2}$) assuming the ligands at lower energy than the metal d orbitals. Thus, in an octahedral arrangement, as for instance in [PtX$_6$]$^{2-}$, the LUMO and the LUMO+1 should have a $\sigma^{*}$ feature according to the traditional rules and are mainly localized on the metal center. Conversely,
the σ bonding combinations are very stabilized in energy, fully populated and with a great contribution from the ligands. Scheme 2 compares the LF and ILF in a O$_h$ symmetry. In the latter case, the two orbitals of the e$_g$ set, namely d$_{x^2-y^2}$ and d$_{z^2}$, could be involved in ILF rather than just one.

**Scheme 2.** Evolution of the electronic structure on increasing the energy of the e$_g$ ligands’ combination for an octahedral transition metal complex

Herein, we will provide a revision of the electronic structure of the octahedral platinum complexes in formal oxidation state IV with one or more metal center(s) surrounded by six halide or chalcogenide ions, among the most electronegative representatives of the periodic table in the perspective of Inverted Ligand Field. This will help to view and rationalize in a new way the reactivity of octahedral platinum complexes that are employed as intermediates in catalysis$^{[16-19]}$ and/or as drugs in medicinal chemistry.$^{[20-27]}$ A case study of application of the ILF to the platinum(IV) reactivity will also be discussed.

**Results and Discussion**

**Chemical bonding in dianionic octahedral species [PtX$_6$]$^{2-}$ with X = halogen**

Octahedral platinum(IV) complexes featuring six equivalent halide ions in the metal coordination sphere are well known, more than 200 X-ray structures containing halides ranging from iodide up to fluoride were found on the Cambridge Crystallographic Database.$^{[28]}$ The first step of the computational analysis was the optimization of the isolated anionic molecular complexes sharing the general formula [PtX$_6$]$^{2-}$ with X = halogen atom at BP86-DFT level of theory$^{[29]}$ with the inclusion of the dispersion forces effects. Zero-Order Regular Approximation (ZORA)$^{[30]}$ for platinum and iodine have been used as implemented in ORCA 5.0 software (more details of Computational Methodology
are shown in SI).\textsuperscript{[31]} To test the occurrence or not of the Inverted Ligand Field,\textsuperscript{[1,5]} we started with a detailed analysis of the electronic structure with particular attention to the metal and ligand contributions to the lowest unoccupied molecular orbital (LUMO) and the closer MOs, taken as a primary diagnostic tool. Figure 1 shows the plots of the antibonding LUMO and the LUMO+1 of the diegative anionic species [PtI\textsubscript{6}]\textsuperscript{2-} and the corresponding bonding counterparts at very low energy, being the HOMO-18 and HOMO-19, together with the relative metal/ligands contribution.

**Figure 1.** LUMO and LUMO+1 $\sigma^*$-bonding and occupied molecular orbitals with a large contribution from d platinum orbitals. The percentages of the metal vs. ligands contribution are reported in round brackets.

The LUMO and the LUMO+1 have a $\sigma^*$ antibonding character with a strong contribution from the six ligands larger than 70% ca. and less the 30% from platinum. The five d orbitals are filled and localized at low energy ($d_{xz}$, $d_{yz}$ and $d_{xy}$) with the $d_{x^2-y^2}$ and $d_{z^2}$ closing the series, being the HOMO-18 and HOMO-19, respectively. The latter are mainly involved in the $\sigma$ bonding counterparts of the LUMO and LUMO+1 orbital being the metal contribution of 63% and only 37% from the ligands. By climbing along the 17\textsuperscript{th} group, thus increasing the electronegativity of the halide up to chloride, the relative order of the orbitals shown in Figure 1 remains unaltered, although the contributions from the metal or the group of the ligands vary in a consistent trend. While for the bromine case the ILF occurrence has been also ascertained, chlorine represents a limiting case being the platinum contribution close to 40% (39.1%) to LUMO and LUMO+1. In all cases, the Inverted Ligand Field could be reasonably invoked rather than the classic Ligand Field, once again confirming the d$^{10}$ metal configuration with a strong covalency of the Pt-halide bonds also in combination with electronegative elements such as chlorine. The situation drastically changes when the platinum is combined with fluoride ligands, the most electronegative element of the Periodic table. In this regard, the LUMO
and LUMO+1 become mainly centered on the metal with contribution around 60% and the corresponding bonding combinations on the fluoride ligands, approaching the classic Ligand Field description. By fitting the electronegativity of the halide vs. the contribution of the metal to the lower empty molecular orbitals (LUMO and LUMO+1), a linear interpolation, shown in Figure 2, has been obtained with a R value very close to one, suggesting a linear dependence of the ILF occurrence on the electronegativity of the halides. The larger is the halide electronegativity and the more stabilized become the ligands’ combination, thus less probable is the occurrence of the ILF.

![Figure 2: Linear dependence of the platinum contribution (%) to the LUMO and LUMO+1 by the electronegativity of coordinated halides.](image)

To provide further validation of the proposed model, we focused our attention on the electronic structure of the trinuclear compound \([\text{Pt}_3\text{Br}_{12}]^{2-}\) featuring platinum centers in both octahedral and square planar coordination environments.\(^{32}\) As shown in the upper part of Figure 3, two bromine of each of the lateral octahedral units bridge the central metal atom, which attains a square planar arrangement. Based on the Ligand Field Theory, \([\text{Pt}_3\text{Br}_{12}]^{2-}\) could be described as a mixed valence compound with a formal oxidation state IV for the platinum atoms in octahedral environment and II for the central one. The optimized structure nicely reproduces the crystallographic one except for an overestimation of the Pt-Br distances no larger than 0.05 Å (the average experimental values are reported in brackets) and a somewhat distortion of the structure from the planarity.
Figure 3. Upper part: Optimized structure of [Pt$_3$Br$_{12}$]$^{2-}$ (the experimental values are reported in brackets). Lower part: lowest unoccupied orbitals with the corresponding metal/ligands contribution in round brackets.

All the lowest unoccupied molecular orbitals, shown in the lower part of Figure 3, are mainly localized on the bromide ligands with a lower contribution from the metal. LUMO and the LUMO+1 feature the in-phase and out-of-phase combinations of the metal d$_{x^2-y^2}$ while LUMO+2 and LUMO+3 are the corresponding combinations of the Pt d$_{z^2}$ orbitals. In any case, the metal contributions are always lower than 37%. LUMO+4 is otherwise mainly localized on the central square planar complex with a 42.7% contribution from d$_{x^2-y^2}$ metal center, which should be empty in the case of a d$^8$ configuration. Thus, the electronic structure analysis provides a substantial support of the questionable assignment of the oxidation state IV to the octahedral platinum centers and highlights a somewhat degree of covalence of the Pt(square planar)-Br linkages.

Chemical bonding in dianionic octahedral species featuring six chalcogenides

Once ascertained that the only exception to the ILF description for the octahedral platinum complexes with six halides is [PtF$_6$]$^{2-}$, the complexes associated with six chalcogen atoms have been investigated. The occurrence of the Inverted Ligand Field in gold compounds associated with chalcogens has been already pointed out some years ago in the unique gold mineral calaverite, AuTe$_2$. The mineral exhibits a CdI$_2$-type structure with the Te atoms between triangles of gold with the presence of direct Te-Te interactions (3.20 Å). The electronic structure of such a crystal has been largely debated since, according to the classic rules, an oxidation state II could be assigned to the gold centers. In this regard, the unusual paramagnetic d$^0$ gold configuration has been hypothesized to evolve through a spontaneous charge disproportionation to d$^{10}$ and d$^8$ configurations. In any case, a recent detailed spectroscopic analysis as well as computational methods solved the dilemma since the different gold
centers are equivalent with a d^{10} configuration while electronic holes are localized on the ligands rather than on the metals. Such a description of the electronic distribution of the calaverite perfectly fits with the ILF one. Conversely to the case of gold, platinum octahedral isolated complexes featuring ligands formed by only chalcogen atoms are known for the sulfur and selenium species. The first step of the computational investigation of the platinum chalcogenides started with the analysis of the electronic structure of the dianionic octahedral species of [Pt(Se_{4})_{3}]^{2-} and [Pt(S_{5})_{3}]^{2-} featuring the metal center surrounded by three η²-Se₄⁻ [34] or S₅⁻ [35] ligands. The optimized structures of the selenium and sulfur platinum complexes are shown in Figure 4.

The optimized structures well reproduce the X-ray ones except for an overestimation of the Pt-chalcogen distances not larger than 0.03 Å. In particular, in the [Pt(Se_{4})_{3}]^{2-} case the experimental Pt-Se distances are in 2.48-2.51 Å range while for [Pt(S_{5})_{3}]^{2-} are between 2.38 and 2.42 Å. Similarly, to the halide cases, the electronic structure of the compounds highlighted the complete occupancy of the five d orbitals of platinum with a small metal contribution in the lowest unoccupied orbitals, once again in contrast with the fundamentals of the Ligand Field theory. In particular, Figure 5 shows the LUMO and LUMO+1 of the [Pt(Se_{4})_{3}]^{2-} complex together with the platinum contribution from d_{x²-y²} and d_{z²}, respectively not larger than 18%. A similar situation occurs in the sulfur complex [Pt(S_{5})_{3}]^{2-} although the percentage contribution from the platinum in LUMO and LUMO+1 slightly increases up to 23%, always remaining in the ILF framework.
Figure 5. Lowest Unoccupied molecular orbitals LUMO and LUMO+1 of $[\text{Pt(Se}_4]_2^2$ complex together with the metal d orbital contribution.

For the sake of comparison, the electronic structure of an octahedral platinum complex featuring six oxygen-based ligands has been examined. In the absence of complexes featuring ligands only formed by oxygen atoms, the dianionic species $[\text{Pt(CF}_3\text{COO)}_6]_2^2$ with six trifluoroacetate moieties has been chosen.$^{[36]}$ Conversely to the precedent cases with selenium and sulfur, the contribution of platinum to the lowest unoccupied orbitals LUMO and LUMO+1 (shown in Figure S1) becomes as large as 50.4 %, suggesting a pure covalent Pt-O bonding with an electronic situation halfway between the classic LF and the ILF description. Thus, similarly to the halogen cases, the more electronegative is the involved chalcogen, the most stabilized become the ligands-based combinations and the more covalent becomes the bond or, in the limiting cases, the LF.

Understanding the electronic structure of the isolated octahedral platinum complexes with chalcogen ligands acquires particular importance in view of the great interest of material science toward the 10th group Transition Metal Dichalcogenides, TMDs. These materials feature a layered structure with the metal centers in an octahedral environment and each chalcogen bridging three different platinum centers. The closeness in energy between the metal d orbitals and the valence p ones of the chalcogen is particularly intriguing since, by changing the nature of the chalcogen element, a drastic variation of the electronic properties of the material may occur. For example, PtTe$_2$ behaves as a metal, PtSe$_2$ is a semimetal while PtS$_2$ is a semiconductor. Pumera et al.$^{[37]}$ pointed out how the electronic properties as well as the photocatalytic properties of the 10th group TMDs are particularly affected by the nature of the chalcogen. XPS experiments revealed no reasonable peaks for Pt(IV) in PtTe$_2$ and PtS$_2$ suggesting an oxidation state of about 0 for the tellurium species and with the prevalence of Pt(II) in PtS$_2$. In this regard, the ILF model could be reasonable invoked in such solid-state structures and the obtained results perfectly agree with those obtained by Whangbo, Jobic et al.$^{[38]}$ who considered improbable the assignment of a formal oxidation state IV to platinum when associated to
tellurium. For solid state systems, the bottom part of the conduction band could provide useful hints on the electronic structure, especially from the analysis of the metal contribution analogously to the LUMO in the molecular systems. The quantitative contribution was estimated based on the Density of State plots of the PtTe₂, PtSe₂, PtS₂ and PtO₂, similarly to those obtained by Jobic et al. and shown in Figure S2. The obtained trends perfectly agree with the ones obtained on molecular systems, the most electronegative is the chalcogen and the larger is the metal contribution to the bottom part of the conduction band, thus the more appropriate description becomes a covalent one. This is evident in the case of the oxygen atom where the metal and oxygen contributions are 58 and 42 %, respectively.

**Inverted Ligand Field in a reactivity: A case study.**

Having the analyses highlighted how the assignment of the oxidation state IV is somewhat inappropriate for the octahedral platinum complexes, we want to reconsider in the framework of the Inverted Ligand Field theory one reaction that commonly involves platinum in the formal oxidation state IV. In particular, the activation of the chalcogen/halogen Se-Cl bonding of PhSe-Cl by a square platinum complex [Pt{CH(CO₂Me)(CN)}₂(Bu₂-bipy)] (Bu₂-bipy = 4,4'-di-t-butyl-2,2'-bipyridine), shown in Scheme 3, has been investigated providing the octahedral species [Pt{CH(CO₂Me)(CN)}₂(Bu₂-bipy)(SePh)(Cl)], with a variation in the oxidation state of the platinum from II in the square planar to IV in the hexa-coordinated. A simplified model of the real complex using the bipyridine moiety in place of the t-butyl one has been used for the calculations.

![Scheme 3](image)

**Scheme 3.** Study reaction of Se-Cl addition to a square planar platinum complex.

In view of the results and being the electronegativity of the elements bound to the metal center smaller than that of oxygen and fluorine, the occurrence of the ILF could be easily predicted for the octahedral product [Pt{CH(CO₂Me)(CN)}₂(bipy)(SePh)(Cl)]. In this regard, LUMO+1 and LUMO+2 empty σ* molecular orbitals, shown in Figure S3, feature a platinum percentage contribution of 26.4 and 31.1%, respectively. A similar electronic distribution has been found also in the starting square planar complex [Pt{CH(CO₂Me)(CN)}₂(bipy)]. According to the classic Ligand Field Theory, the dₓ²-y² orbital in [Pt{CH(CO₂Me)(CN)}₂(bipy)] should be empty and largely contribute to the σ* interaction
(thus to the LUMO+3 in the present case, being the LUMO-LUMO+2 centered on the bipyridine ligand). The $d_{x^2-y^2}$ calculated contribution to LUMO+3 is instead lower than 29.0% while the corresponding bonding orbital is metal centered. Thus, the precursor features a d$^{10}$ configuration, in agreement with a ILF description.

The study of the interaction between [Pt(CH(CO$_2$Me)(CN))$_2$(bipy)] and the PhSe-Cl substrate allows the detection of the intermediate [Pt(CH(CO$_2$Me)(CN))$_2$(bipy)]*PhSe-Cl with a free energy gain of -10.9 kcal mol$^{-1}$. The optimized geometry of the adduct [Pt(CH(CO$_2$Me)(CN))$_2$(bipy)]*PhSe-Cl is shown in Figure 6 with a quasi linear Pt---Se---Cl arrangement, the angle being 172°. The Se-Cl distance is 0.16 Å elongated compared to the isolated system (2.39 vs. 2.23 Å). The aryl substituent of PhSe-Cl is involved in weak interactions with the bipyridine ligand of the complex. The chloride release provides the cationic intermediate [Pt(CH(CO$_2$Me)(CN))$_2$(bipy)(SePh)]*, shown in Figure 6, with a free energy cost of +19.2 kcal mol$^{-1}$. The presence of a peripheral carbonyl group in CH(CO$_2$Me)(CN) ligand allows the formation of an octahedral intermediate rather than a pentacoordinated one with the sixth coordination site occupied by the oxygen. The substitution of the coordinated oxygen with the chloride occurs with a free energy gain as large as -31.7 kcal mol$^{-1}$.

![Figure 6](image_url)

**Figure 6.** Optimized structure of adduct [Pt(CH(CO$_2$Me)(CN))$_2$(bipy)]*SePhCl and cationic species [Pt(CH(CO$_2$Me)(CN))$_2$(bipy)(SePh)]$^+$. The analysis of the electronic structure of the [Pt(CH(CO$_2$Me)(CN))$_2$(bipy)(SePh)]$^+$ intermediate revealed the occurrence of the ILF with the metal contribution to the LUMO and LUMO+1 less than 35%. The latter contribution is somewhat larger than that found in the final octahedral species [Pt(CH(CO$_2$Me)(CN))$_2$(bipy)(SePh)(Cl)] possibly due to the oxygen coordination. To better
understand the electronic structure of the cationic intermediate, a simplified model \([\text{Pt}\{\text{CH(Me)}(\text{CN})\}_2(\text{bipy})(\text{SePh})]\)^+ has been optimized obtaining a square pyramidal intermediate. The resulting LUMO, shown in Figure 7, features a strong contribution from the apical SePh ligand and only 32.4 \% from the metal, suggesting once again the ILF occurrence.

![Figure 7. LUMO orbital of the simplified model [Pt{CH(Me)(CN)}_2(bipy)(SePh)]^+.](image)

The occurrence of the Inverted Ligand Field in all the steps of the reaction allows to conclude that hardly platinum is involved in an oxidative process but more probably it maintains the \(d^{10}\) configuration with a somewhat efficient \(\sigma\) back-donation toward the ligands.

**Conclusions**

The occurrence of ILF has been shown also for the formal IV oxidation state in octahedral platinum complexes. For the iodide, bromide and chloride, the energy of the \(d\) metal orbitals are lower than the \(“e_g”\) combination of the ligands and a \(d^{10}\) configuration or Pt(0) oxidation state describes better the complexes. Only for the fluoride, a IV oxidation state is archived. The metal contribution in the antibonding \(e_g\) combinations of the halogen complexes is in correlation with the halogen electronegativity.

For the elements in the chalcogenide group, the ILF are found for sulfur and selenium complexes as a consequence of a ligand centered antibonding \(e_g\) sets. In the case of oxygen, a strong covalent character of the Pt-O bonds has to be invoked, being the antibonding \(e_g\) sets occupied at almost 50\% for the metal and the ligand.

The oxidative activation of a Se-Cl bond by a square planar Pt(II) complex has been reconsidered in the framework of ILF. Interestingly, in the starting, the final octahedral as well as the intermediate complexes, the Pt metal has a \(d^{10}\) configuration and the whole process could be properly classified as not oxidative process.
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Keywords

Inverted Ligand Field; Electronic Structure; Oxidative Addition; Platinum complexes

References