Inverted Ligand Fields

What is The Deal With Copper(III)?

MacMillan Group Meeting
June 15th, 2020
Cesar Nicolas Prieto Kullmer
Outline of Talk

Bonding Models of Coordination Complexes and Their Pitfalls — What are Inverted Ligand Fields?

Early Experimental and Computational Evidence for Inverted Ligand Fields

Copper (III) Complexes — Theoretical and Experimental Analysis of their Electronic Structure

The Implications of Inverted Ligand Fields for Organometallic Complex Reactivity
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Crystal Field Theory

**d—orbitals:**

- $d_{xy}$
- $d_{xz}$
- $d_{yz}$
- $d_{z^2}$
- $d_{x^2-y^2}$

**Free ion d-orbitals**

- Relies only ligand—metal electronic repulsion
- Cannot account for neutral ligands
- Fails to predict certain ligand effects (i.e. OH$^-\text{ vs. } H_2O$)
- Only considers d—orbitals

Ligand Field Theory

Factors in ALL metal orbitals and ALL ligand orbitals

- returns same splitting of d-orbitals as CFT
- rationalizes neutral ligand bonding and complex stability
- **assumption**: ligand orbitals considered lower in energy

Complete MO diagram

MO Shape and Composition

$\psi_{\text{anb}} = c_1 \psi_1 - c_2 \psi_2$

MO composition reflects individual AO contribution

$\psi_{\text{bon}} = c_1 \psi_1 + c_2 \psi_2$

non-polarized

$\psi_{\text{anb}}$

$\psi_{\text{bon}}$

polarized

$\psi_{\text{anb}}$

$\psi_{\text{bon}}$

Elelrons of MO reside mostly on main contributor

Oxidation State Formalism

According to the IUPAC:
OS of an atom is the charge of this atom after ionic approximation of its heteronuclear bonds.

Why?
…underlying principle is that the ionic sign in an AB molecule is deduced from the electron allegiance in a LCAO-MO model:
The bond’s electrons are assigned to its main atomic contributor.

tend to assign oxidation state based on electronegativity

What if combined ligand contributions outweigh metal?

ESR hyperfine coupling w/ chlorine observed
• e− hole 3% of time on any chlorine (18% total)

What is an inverted ligand field?

- Inverted ligand fields show abnormal MO orderings and compositions.
- HOMO and LUMO are ligand-based rather than metal-based.
- Electrons do not reside on atoms as one would expect from oxidation state formalism.

What is an inverted ligand field?

<table>
<thead>
<tr>
<th>Normal splitting</th>
<th>Inverted splitting</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oh</td>
<td></td>
</tr>
<tr>
<td>$t_{2g}$</td>
<td>$e_g$</td>
</tr>
<tr>
<td>$e_g$</td>
<td>$t_{2g}$</td>
</tr>
<tr>
<td>Td</td>
<td></td>
</tr>
<tr>
<td>$t_{2}$</td>
<td>$e$</td>
</tr>
<tr>
<td>$e$</td>
<td>$t_{2}$</td>
</tr>
<tr>
<td>D$_{4h}$</td>
<td></td>
</tr>
<tr>
<td>$b_{1g}$</td>
<td>$b_{2g}$</td>
</tr>
<tr>
<td>$a_{1g}$</td>
<td>$e_g$</td>
</tr>
<tr>
<td>$e_g$</td>
<td>$b_{1g}$</td>
</tr>
<tr>
<td>$a_{1g}$</td>
<td>$b_{2g}$</td>
</tr>
</tbody>
</table>

Ir$^{4+}$ + 6 Cl$^-$

Ir$^{2+}$ + 5 Cl$^-$ + 1 Cl$^+$

Ir$^{0+}$ + 4 Cl$^-$ + 2 Cl$^+$

Ir$^{-2}$ + 3 Cl$^-$ + 3 Cl$^+$

e etc.
A Theoretical Inverted Octahedral Ligand Field

M = 6 e⁻  normal MO diagram  L = 12 e⁻

M = 10 e⁻  inverted MO diagram  L = 8 e⁻

only some MOs switch their order
the metal—centered MOs change their identity
Approaches to Ligand Field Inversion

lower metal-based orbitals
charged metal center
more electronegative metal

raise ligand-based orbitals
electron-releasing substituents
more electropositive elements

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Solid containing formally Ag(III):

- Ag—F bonding (−6.5 to −9.0 eV): dominant Ag d—orbital contribution
- Ag—F anti bonding (−0.7 eV): excess F 2p—orbital contribution

... classical picture used for ionic inorganic compounds ... an ionic formulation of KAgF$_4$ as K$^+Ag^{III}(F^-)_4$, must be modified in this case...
Early Evidence — $[\text{Ni}(\text{SnPh}_3)(\text{np}_3)]^+$

- $[\text{Ni}(\text{np}_3)]$ known to exist independently as a stable complex
- Donor–acceptor relationship between Ni and Sn inverted ($\sigma$-SnPh$_3$ ~ 2eV higher than $2a_1$)
- Metal is best described as $d^{10}$ with SnPh$_3^+$ ligand

$\sigma$-noninnocence: ambiguity on which atom is acting as the donor

Early Evidence — Vitamin B<sub>12</sub> mimetics

- Modulation of Co—N distance affects propensity metal to undergo inner-sphere e⁻ transfer
- Intermediate Co—N distance shows avoided crossing at longer Co—C distances (allows for Co—C homolysis)

\[ \sigma_1 \text{ — NH}_2, \ z^2 \text{ bonding} \]
\[ \sigma_2 \text{ — } p_z, \ \text{CH}_3 \text{ bonding } + \text{NH}_2, \ z^2 \text{ antibonding} \]
\[ \sigma_3 \text{ — } p_z, \ \text{CH}_3 \text{ antibonding } + \text{NH}_2, \ z^2 \text{ antibonding} \]
**Computational Investigation of $d^{10}$**

- **Using $EH_3$ (E = N, P, As, Sb, Bi), M = Ni, Pd, Pt:**

  Inherent instability (decay into $ML_2 + 2L$) limits combinations to local minima

  Donor ability of ligand does not correlate w/ electropositivity (inert electron pair effect)

  Varying metal did not return clear result due to realities of atomic orbital energies

- **Using $L = X^−, PH_3$, $M = Zn^{2+}$:**

<table>
<thead>
<tr>
<th>Orbital</th>
<th>$[ZnF_4]^{2−}$ Energy(eV)</th>
<th>%Zn</th>
<th>%F</th>
<th>$<a href="BF_4">Zn(PH_3)_4</a>_2$ Energy(eV)</th>
<th>%Zn</th>
<th>%L</th>
</tr>
</thead>
<tbody>
<tr>
<td>$2t_2$</td>
<td>0.87</td>
<td>16</td>
<td>84</td>
<td>11.03</td>
<td>8</td>
<td>92</td>
</tr>
<tr>
<td>$1a_1$</td>
<td>−1.70</td>
<td>19</td>
<td>81</td>
<td>14.13</td>
<td>46</td>
<td>54</td>
</tr>
<tr>
<td>$1e$</td>
<td>−2.86</td>
<td>92</td>
<td>8</td>
<td>17.73</td>
<td>99</td>
<td>1</td>
</tr>
<tr>
<td>$1t_2$</td>
<td>−3.14</td>
<td>82</td>
<td>18</td>
<td>17.79</td>
<td>96</td>
<td>4</td>
</tr>
</tbody>
</table>

Inversion with a true transition metal

$\text{[Rh(AlMe)$_4$]}^+$

formally Rh(I)
effectively Rh(−I)

bending

MeAl
MeAl
MeAl
AlMe
AlMe

$e_g$ (xz, yz) rehybridizes to form orbitals with significant lone-pair character

d $\text{ECR}_3$ ligands

highly electropositive
strong π acceptors
synthetically accessible

Can we see a similar effect in homoleptic hexacoordinate AlMe complexes?

Mo(AlMe)$_6$

also optimizes into a trigonal prismatic structure
Inversion with a true transition metal

Mo(AlMe)₆
formally Mo(0)
effectively Mo(−IV)

π—acidity of ligands crucial to stability

Pd(AlMe)₄
formally Pd(0)
effectively Pd(0)

removal of e− from Pd to Rh occur from ligand over metal

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The Snyder Hypothesis

Snyder presumed that upon oxidation of \([\text{Cu(CF}_3]^3\text{−}]\) a ligand is oxidized.

MO diagram implies that only four bonding electrons hold this complex together.

both HOMO and LUMO ligand-based

Snyder’s description: \([\text{CF}_3^− \text{Cu}+ \text{CF}_3^−]\)

DFT calculations reveal:

atomic charges: Cu (+0.71), C (+0.74), F (-0.39)
d population: \(d_{xy}, d_{xz}, d_{yz}, d_{x^2-y^2}\) 1.96 — 1.98, \(d_{x^2-y^2}\) 1.77

CF\(_3\) groups carry 25.4 electrons (3CF\(_3^−\) + CF\(_3^+\))

- bonding is principally ionic and accompanied by two 5c/2e− bonds
- depletion delocalized across all CF\(_3\) ligands
- copper is best described as a Cu(I) species

The Snyder Hypothesis — Backlash

... Snyder has confused two important but fundamentally different concepts: the formal oxidation state, and partial charges as obtained, for example, from population analysis ...

- interprets filled d—orbitals as signs of Cu—C covalency

- invokes square—planar geometry as tell-tale sign of normal ligand field


... designation of a formal oxidation state is entirely arbitrary ... uncritical application of the resulting oxidation values can lead to confusing and physically unrealistic descriptions for organic, organometallic, and inorganic species alike ...

- interprets high ionic bonding as sign that electrons do reside in d—orbitals

- ascribes copper a d^{10} configuration and a NONFORMAL Cu(I) oxidation state

Comparing $[\text{Cu(CF}_3\text{)}_4]^n$

20 years later ...

geometry defined by higher energy, ligand—based orbitals

Cu(I) shows IFL when forced into D$_{2d}$ symmetry

Ligand geometry influences ligand field inversion

$[\text{Cu(CF}_3\text{)}_4]^{-}$
$\text{Cu(III)}$

$[\text{Cu(CF}_3\text{)}_4]^2^{-}$
$\text{Cu(II)}$

$[\text{Cu(CF}_3\text{)}_4]^3^{-}$
$\text{Cu(I)}$

Ligand Oxidation in \([Cu(CF_3)_4]^-\)

**Ligand Geometry and Spatial Arrangement**

- Optimized \([Cu(CF_3)_4]^3-\): \(d(C-F) = 1.37\), \(F-C-F\) angle of 105°
- Optimized \([Cu(CF_3)_4]^3-\): \(d(C-F) = 1.44\), \(F-C-F\) angle of 100°

**Energetics of Ligand Oxidation**

- **Grushin’s method:**
  
<table>
<thead>
<tr>
<th>Reaction</th>
<th>Products</th>
<th>(\Delta E) (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(T_d- [Cu(CF_3)_4]^3- + I_2)</td>
<td>(SP-[Cu(CF_3)_4]^- + 2I^-)</td>
<td>(-97)</td>
</tr>
<tr>
<td>(CF_3^- + I_2)</td>
<td>(CF_3^+ + 2I^-)</td>
<td>(+24)</td>
</tr>
<tr>
<td>(CF_3^+ + I^-)</td>
<td>(CF_3I)</td>
<td>(-74)</td>
</tr>
<tr>
<td>(T_d- [(CF_3)_4]^4-)</td>
<td>(SP-[(CF_3)_4]^4-)</td>
<td>(+109)</td>
</tr>
<tr>
<td>(SP-[(CF_3)_4]^4- + I_2)</td>
<td>(SP-[(CF_3)_4]^2^- + 2I^-)</td>
<td>(-221)</td>
</tr>
<tr>
<td>(T_d- [(CF_3)_4]^4- + I_2)</td>
<td>(SP-[(CF_3)_4]^2^- + 2I^-)</td>
<td>(-111)</td>
</tr>
</tbody>
</table>

Combined Computational Evidence

$[\text{Cu(CF}_3\text{)}_4]^-$ has an inverted ligand field and mainly ligand—centered FMOs

Energetics and Ligand Geometry support the existence of a CF$_3^+$ ligand in the coordination sphere

Coordination geometry influences ligand field inversion due to inter—ligand interactions

*How can we prove this experimentally?*
Combined Computational Evidence

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How can we prove this experimentally?
Synchrotron-based X-Ray Spectroscopy — A Primer

- relies on electronic excitation from core orbitals (e.g. 1s, 2s, 2p)
- element-specific orbital energy separations provide molecular/electronic information
- can focus on absorption (XAS) or emission (XES)
- requires access to synchrotron light source

ALBA synchrotron (Cerdanyola del Vallés)

Synchrotron Radiation

Radiation that occurs when charged particles are accelerated in a curved path

\[
P = \frac{2Ke^2}{3c^3} \left[ \frac{\gamma^2 v^2}{r} \right]^2 = \frac{2Ke^2\gamma^4v^4}{3c^3r^2}
\]
**Edges in Core Spectroscopy**

- **Pre-edge**: Excitation of core electron to bound state
- **EXAFS**: Photoelectron scattering interference patterns
- **Rising edge**: Mixture of transitions to bound states and near-edge scattering

Transitions follow **selection rules**:

\[ \Delta L = 1, -1 \]
\[ \Delta S = 0 \]
Synchrotron-based X-Ray Spectroscopy — A Primer

X-ray absorption spectroscopy

- **Metal K-Edge XAS**: Excitation from metal 1s.
  - Pre edge normally assigned as 1s - nd transitions (forbidden)
  - Ligand p orbital admixture raises intensity
- **Ligand K-Edge XAS**: Excitation from ligand 1s.
  - Excitations into ligand p orbital common (allowed)
  - Metal d-orbital admixture attenuates intensity
- **Metal L_{2,3}-Edge XAS**: Excitation from metal 2p.
  - Metal 2p -> 3d transition allowed, attenuated by ligand p admixture
  - Yields two edges. Rel. inten. modulates by SO coupling/Auger effects.

X-ray emission spectroscopy

- **Kα XES**: Decay into 1s from 2p.
  - Two final 2p\(^5\) states yield two features (Kα\(_1\) and Kα\(_2\))
- **Kβ XES**: Decay into 1s from 3p.
  - Exchange interaction w/ unpaired 3d splits line (Kβ\(^+\) and Kβ\(_{1,3}\))
- **RIXS**: Excite w. energies that match transition to bound states and study temporal evolution of electronic state via emission.

Inverted d$^{10}$ favors D$_{4h}$ over T$_d$ in angular overlap approximations of MOs.

- UV-vis should show d-d band in d$^8$ limit — not observed
- d—d band unlikely to be buried under CT band as this would imply a very large field splitting

Experimental Verification of the IFL in [Cu(CF$_3$)$_4$]$^-$

**Cu K-edge XAS**

1s—4p

MLCT? 1s—3d? 1s—4p?

3d$^8$ K edge $\rightarrow$ 1s$^1$3d$^9$ Ka $\rightarrow$ 1s$^2$2p$^5$3d$^9$

3d$^{10}$ K edge $\rightarrow$ 1s$^1$3d$^{10}$L$^1$ Ka $\rightarrow$ 1s$^2$2p$^5$3d$^{10}$L$^1$

3d$^{10}$ K edge $\rightarrow$ 1s$^1$3d$^{10}$4p$^1$ Ka $\rightarrow$ 1s$^2$2p$^5$3d$^{9}$4p$^1$

- Cross peak observed for 8982 eV, results from concurrent 1s—4p excitation due to broad bandwidth

- Corrected peak at 8982 eV shows no cross peak, which excludes 1s—3d transition, and supports d$^{10}$ assignment

interorbital exchange interactions proportional to proximity of radial probability maxima (significant only for 2p—3d exchange)
Experimental Verification of the IFL in [Cu(CF\textsubscript{3})\textsubscript{4}]$^{-}$

- Inverted d\textsuperscript{10} is predicted with all applied levels of theory
- Unoccupied 2b\textsubscript{2} orbital is mostly of CF\textsubscript{3} character (%CF\textsubscript{3} = 58.9—63.8)
- No d—d transition predicted (confirms UV—vis)
- K-edge XAS feature at 8982 eV identified as 1s—CF\textsubscript{3}\sigma^*, confirms other peak energies and assignments

TDDFT and ROCIS show high fidelity XAS transition estimation and allow for accurate designation of L\textsubscript{2,3} edge features in copper systems

The Myth of $d^8$ Copper(III)

- Cu L$_{2,3}$-edge XAS affords a direct means to estimate Cu 3d orbital contributions to vacant frontier MOs

- L$_{2,3}$ main lines correspond to the 2p $\rightarrow$ LUMO excitation

- LUMO w/ ligand parentage disallows this transition ($\Delta L = 0$)

**all Cu$^{III}$ compounds show less than 50% d-character in LUMO**

*tell-tale sign of ligand field inversion and $d^{10}$ configuration*
computational model can be applied to other formally copper(III) compounds

all except one show inverted ligand field
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Electrophilic Reactivity of $[\text{Cu(CF}_3)_4]^-$

Some computation on $S_n^2$ reactivity has been done:

$[\text{Cu(CF}_3)_4]^-$ + $\text{PH}_3 \xrightarrow{\Delta G = +47 \text{ kcal/mol}} [\text{Cu(CF}_3)_3]^{2^-} + \text{H}_3\text{PCF}_3^+$

$[\text{Cu(CF}_3)_4]^-$ + $\text{F}^- \xrightarrow{\Delta G = -29 \text{ kcal/mol}} [\text{Cu(CF}_3)_3]^{2^-} + \text{CF}_4$

suffers from high activation energy ($\Delta G^\dagger = +56 \text{ kcal/mol}$)

inverted field complexes as sources of electrophilic reactants is currently underexplored
Impact on Copper-Catalyzed Nitrene Transfer

Crystal structure reveals dearomatized aryl moiety on nitrene

XAS points towards the hole being located on the nitrogen

Reactivity posited to stem from electron-deficient nitrogen

Peroxo-Bridged Dicopper(II) Complexes

Coupled binuclear copper (CBC) proteins: Bind dioxygen for a variety of biological functions

Hemocyanin  Catechol oxidase  Tyrosinase

peroxo (P) \[ \text{L}_n\text{Cu}^{\text{II}} \text{O}_2 \text{Cu}^{\text{II}}\text{L}_n \] \[ \text{L}_n\text{Cu}^{\text{III}} \text{O}_2 \text{Cu}^{\text{III}}\text{L}_n \] μ—oxo (O)

- L\text{2,3}—edge area reveals 40% Cu 3d-character in the SOMO
- Electron-deficient O\text{2—} a highly oxidizing species that drives the reactivity of the complexes

\[ \text{ONa} \]

\[ \text{[Cu}_2(\text{O}_2)(\text{DBED})_2]^{2+} \]

acetone, −90°C

\[ \text{OH} \]

Impact on Reductive Elimination — Copper(III)

Possible Mechanisms

Direct RE:
\[ \Delta H = -53.6 \]
\[ \Delta H^\ddagger = 19.7 \]

Homolysis:
\[ \Delta H = 12.5 \]
\[ \Delta H^\ddagger = 12.6 \]

Abstraction:
\[ \Delta H = -66.1 \]
\[ \Delta H^\ddagger = 41.1 \]

CF\(_3\) dissociation:
\[ \Delta H = 27.4 \]

F\(^-\) ejection:
\[ \Delta H = 35.9 \]

Population Analysis of Direct RE

Impact on Reductive Elimination — Nickel(IV)

**Intrinsic Bond Orbitals (IBO)**

- complex better described as Ni(II) w/ cationic aryl ligand
- cationic aryl conflicts with Hammett analysis ($\rho = -0.91$)
- e$^-$ flow supports nucleophilic attack of CF$_3^-$ on Ph$^+$
- TS shows Ni acting as LA activating $\pi$—system and interaction increases w/ electron-donating substituents

$\sigma$-noninnocence-induced masked aryl cation transfer

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Copper(III) — IFLs as Periodic Trend

\[
\begin{align*}
[Cu(CF_3)_4]^- & \quad \text{[Ga(CH}_3)_4]^+ \\
\text{b}_{1g} & \quad \text{b}_{1g} \\
\text{29% d} & \quad \text{7% d}
\end{align*}
\]

- d—orbitals become contracted across a period
- main—group bonding treats d—orbitals as core orbitals
- transition—metal bonding treats d—orbitals as valence orbitals

IFLs reside at the transition of transition—and main—group bonding formalisms

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Questions?

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