d-Orbital Energy Levels in Planar $[M^{II}F_4]^{n-}$, $[M^{II}(NH_3)_4]^{n+}$ and $[M^{II}(CN)_4]^{n-}$ Complexes: The Nature of M-L π Bonding and the Implications for Ligand Field Theory

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Supporting Information

Contents

S1: CFT analysis for a planar complex

The electrostatic radial parameters are:

$\alpha_n = Ze^2 \frac{\langle r^n \rangle}{a^{n+1}}$ where <*r*> is the average d orbital radius and *a* is the distance of the point charge from the nucleus.

The crystal field parameters for a general tetragonal D_{4h} complex are:

$Dq = 1/6\ \alpha_4(\text{Eq})$

$Ds = 2/7[\alpha_2(\text{Eq}) - \alpha_2(\text{Ax})]$

$Dt = 2/21[\alpha_4(\text{Eq}) - \alpha_4(\text{Ax})]$

which simplify for a planar complex where the axial parameters are zero and noting that *Dq* and *Dt* are both functions of α_4 to:

$Dq = 1/6\ \alpha_4(\text{Eq})$

$Ds = 2/7\alpha_2(\text{Eq})$

$Dt = 4/7Dq$

The d orbital energies are:

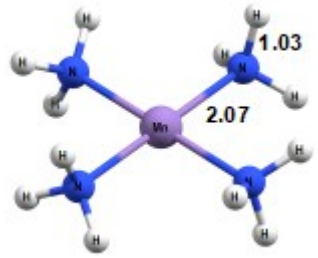
$E(d_{x^2-y^2})$	$= 6Dq + 2Ds - Dt$	$= 5\,{}^{3}\!/_{7}\ Dq + 2Ds$
$E(d_{z^2})$	$= 6Dq - 2Ds - 6Dt$	$= 2\,{}^{4}\!/_{7}\ Dq - 2Ds$
$E(d_{xy})$	$= -4Dq + 2Ds - Dt$	$= -4\,{}^{4}\!/_{7}\ Dq + 2Ds$
$E(d_{xz}/d_{yz})$	$= -4Dq - Ds + 4Dt$	$= -1\,{}^{5}\!/_{7}\ Dq - Ds$

S2: DFT optimisations and AI LFT d orbital energies for $[M(NH_3)_4]^{2+}$, M = Mn, Fe, Co, Ni, Cu

Typical ORCA 3 command line

```
!UKS BP RI def2-TZVP def2-TZVP/J Grid6 NoFinalGrid TightSCF UNO SlowConv Cosmo(water) Opt
```

$[Mn(NH_3)_4]^{2+}$: 2S+1 = 2



(N.B. The optimised structure had a small D_{2d}. These angles were idealised to 180 º for the AI LFT calculations and are the coordinates given below.)

```
Mn      -0.001729000     -0.003546000      0.000029000
N       -1.470005726      1.452108680     -0.006785967
H       -1.711134134      1.746970436      0.949473122
H       -1.205915545      2.316840549     -0.495477977
```

N	1.453244500	1.465657681	0.002772228
H	2.335696392	1.194953853	0.454594058
H	1.714249491	1.737312068	-0.955150169
N	-1.454981806	-1.471012159	-0.002710984
H	-1.727468910	-1.728040944	-0.961520884
H	-2.331858748	-1.205095655	0.462831851
N	1.465054631	-1.457720420	0.006837037
H	1.194686676	-2.340170991	-0.445357278
H	1.731526076	-1.718037518	0.966461396
H	-1.174553415	-2.353870344	0.442457599
H	-2.360954369	1.167021622	-0.432181817
H	1.175740284	2.341456292	0.463401816
H	2.343848953	-1.183146194	-0.449932923

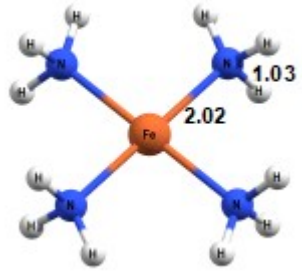
AILFT (Version 3)

B = 0.004295800 a.u. = 0.117 eV = 942.8 cm**-1
C = 0.014507334 a.u. = 0.395 eV = 3184.0 cm**-1 (C/B= 3.38)

The ligand field one electron eigenfunctions:

Orbital	Energy (eV)	Energy(cm-1)	dxy	dyz	dz2	dxz	dx2-y2
1	0.000	0.0	-0.001360	0.001757	-0.999980	0.003773	-0.004529
2	0.087	702.4	0.000028	0.306036	0.004138	0.952009	-0.001864
3	0.089	714.1	0.000018	-0.952017	-0.000508	0.306037	-0.002115
4	0.445	3592.3	0.000761	-0.001435	-0.004524	0.002439	0.999985
5	4.340	35008.0	0.999999	0.000012	-0.001357	-0.000029	-0.000767

$[Fe(NH_3)_4]^{2+}$: 2S+1 = 1



Fe	-0.000938000	-0.001039000	0.000197000
N	-1.414996000	1.439098000	-0.006281000
H	-1.339599000	2.063196000	0.808280000
H	-1.347243000	2.047377000	-0.833489000
N	1.400458000	1.450493000	0.000515000
H	2.374956000	1.129158000	-0.011865000
H	1.315968000	2.075593000	-0.812356000
N	-1.402686000	-1.452894000	0.001892000
H	-1.325496000	-2.068691000	-0.818886000
H	-2.377149000	-1.131227000	0.001885000
N	1.412771000	-1.440963000	0.006517000
H	1.338888000	-2.064149000	-0.808919000
H	1.343270000	-2.050110000	0.832933000
H	-1.325580000	-2.068168000	0.823017000
H	-2.386433000	1.108534000	0.001450000
H	1.330377000	2.056349000	0.829365000
H	2.384323000	-1.110669000	0.000804000

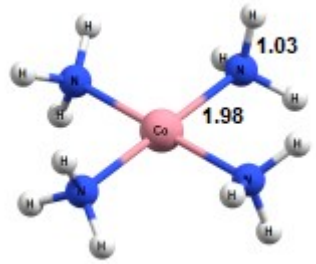
AILFT (Version 3)

B = 0.004521951 a.u. = 0.123 eV = 992.5 cm**-1
C = 0.016476375 a.u. = 0.448 eV = 3616.1 cm**-1 (C/B= 3.64)

The ligand field one electron eigenfunctions:

Orbital	Energy (eV)	Energy(cm-1)	dxy	dyz	dz2	dxz	dx2-y2
1	0.000	0.0	-0.001149	0.003202	-0.999976	0.006060	0.000274
2	0.066	531.7	0.001121	0.264616	0.006690	0.964329	-0.001091
3	0.067	541.6	0.000900	0.964345	0.001483	-0.264628	0.002792
4	0.373	3005.6	0.000694	-0.002405	0.000276	0.001789	0.999995
5	3.987	32159.5	0.999998	-0.001159	-0.001158	-0.000837	-0.000695

$[Co(NH_3)_4]^{2+}$: 2S+1 = 2



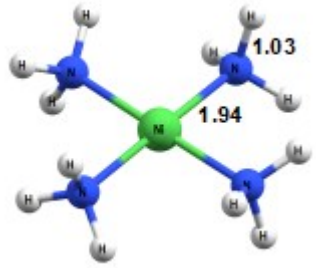
Co	-0.001791000	-0.000843000	0.000868000
N	-1.410854000	1.396567000	-0.002987000
H	-1.668666000	1.686150000	0.950098000
H	-1.138939000	2.257421000	-0.493160000
N	1.395694000	1.408408000	0.001138000
H	2.256634000	1.137701000	0.491839000
H	1.685139000	1.663674000	-0.952677000
N	-1.398035000	-1.411155000	0.003372000
H	-1.673530000	-1.681803000	-0.950327000
H	-2.266546000	-1.135496000	0.477605000
N	1.407956000	-1.397837000	0.002017000
H	1.135015000	-2.263432000	-0.479121000
H	1.670653000	-1.678891000	0.956329000
H	-1.110159000	-2.280940000	0.467897000
H	-2.287348000	1.104664000	-0.452061000
H	1.103867000	2.286065000	0.447975000
H	2.281802000	-1.108367000	-0.453749000

AILFT (Version 3)

```
B               =  0.004953322 a.u. =     0.135 eV =    1087.1 cm**-1
C               =  0.017404754 a.u. =     0.474 eV =    3819.9 cm**-1 (C/B=  3.51)

The ligand field one electron eigenfunctions:
Orbital    Energy (eV)  Energy(cm-1)      dxy        dyz        dz2        dxz        dx2-y2
    1          0.000        0.0        -0.000051   0.002746  -0.999980   0.005639   0.000212
    2          0.038      308.1         0.000062   0.290626   0.006194   0.956814  -0.002196
    3          0.039      316.8        -0.000067   0.956831   0.000989  -0.290631   0.002685
    4          0.284     2292.6         0.000610  -0.001931   0.000223   0.002881   0.999994
    5          3.820    30813.2         1.000000   0.000048  -0.000052  -0.000080  -0.000610
```

$[Ni(NH_3)_4]^{2+}$: 2S+1 = 1



Ni	-0.001739000	-0.000906000	0.000557000
N	-1.380839000	1.366316000	-0.020276000
H	-1.636021000	1.650644000	0.935246000
H	-1.099710000	2.220866000	-0.515345000
N	1.365681000	1.378363000	0.017855000
H	2.219808000	1.098857000	0.514609000
H	1.650984000	1.630182000	-0.938266000
N	-1.368166000	-1.380892000	0.020149000
H	-1.642009000	-1.645465000	-0.935884000
H	-2.228695000	-1.097591000	0.503433000
N	1.378054000	-1.367853000	-0.014285000
H	1.096061000	-2.227824000	-0.499352000
H	1.638361000	-1.642941000	0.942570000
H	-1.071697000	-2.245567000	0.487911000
H	-2.250651000	1.067366000	-0.476757000
H	1.066549000	2.249885000	0.470924000
H	2.244920000	-1.071550000	-0.478030000

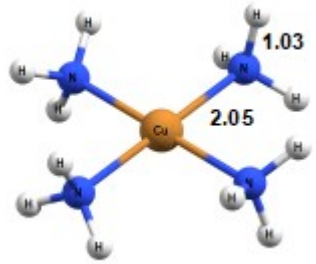
AILFT (Version 3)

```
B               =  0.005402533 a.u. =     0.147 eV =    1185.7 cm**-1
C               =  0.018250726 a.u. =     0.497 eV =    4005.6 cm**-1 (C/B=  3.38)

The ligand field one electron eigenfunctions:
Orbital    Energy (eV)  Energy(cm-1)      dxy        dyz        dz2        dxz        dx2-y2
    1          0.000        0.0        -0.000058   0.011827  -0.999665   0.023014   0.000148
    2          0.009       71.8         0.000045   0.338593   0.025659   0.940582  -0.001352
    3          0.010       79.7        -0.000022   0.940858   0.003332  -0.338780   0.001857
    4          0.308     2485.3         0.000641  -0.001291   0.000176   0.001898   0.999997
    5          3.804    30683.1         1.000000   0.000007  -0.000059  -0.000050  -0.000641
```

$[Cu(NH_3)_4]^{2+}$: 2S+1 = 2

(N.B. The optimised structure had a small D_{2d} distortion. These angles were idealised to 180 º for the AI LFT calculations and are the coordinates given below.)




```
Cu      -0.001451000     -0.000925000      0.000898000
N       -1.457131000      1.442563000     -0.003047000
H       -1.729401000      1.728796000      0.944746000
H       -1.159707000      2.293816000     -0.492721000
N        1.441906000      1.455197000     -0.001061000
H        2.296029000      1.157303000      0.483280000
H        1.722766000      1.729085000     -0.949995000
N       -1.444734000     -1.456973000      0.002857000
H       -1.721905000     -1.736952000     -0.945379000
H       -2.300897000     -1.156969000      0.482264000
N        1.454437000     -1.444620000      0.004843000
H        1.157893000     -2.298080000     -0.481510000
H        1.726016000     -1.726722000      0.954075000
H       -1.138523000     -2.310328000      0.483292000
H       -2.314700000      1.133184000     -0.473832000
H        1.134877000      2.311848000      0.472951000
H        2.312313000     -1.136941000     -0.466502000
```

AILFT (Version 3)

```
The ligand field one electron eigenfunctions:
Orbital    Energy (eV)  Energy(cm-1)      dxy        dyz        dz2        dxz        dx2-y2
    1          0.000        0.0         0.000033  -0.344634  -0.073520  -0.935853   0.001277
    2          0.001        6.4        -0.000245   0.938220   0.006096  -0.345982   0.001598
    3          0.056      448.8        -0.000033   0.031142  -0.997275   0.066877   0.000059
    4          0.349     2815.3         0.000754  -0.001061   0.000143   0.001744   0.999998
    5          3.976    32072.2         1.000000   0.000243  -0.000029  -0.000053  -0.000754
```

S3: DFT optimisations and AI LFT d orbital energies for $[NiL_4]^m$, L = F, NH_3 and CN

Typical ORCA 4 command lines:

```
!RKS BP RI def2-TZVP/C Grid6 NoFinalGrid TightSCF UNO SlowConv Opt
!CPCM(water)
!KDIIS
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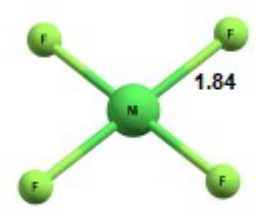
$[NiF_4]^{2-}$: 2S+1 = 1



Ni	0.000000000	0.000000000	0.000000000
F	1.840529000	0.000000000	0.000000000
F	-1.840529000	0.000000000	0.000000000
F	0.000000000	1.839215000	0.000000000
F	0.000000000	-1.839215000	0.000000000

AILFT (ORCA 4)

Racah Parameters :

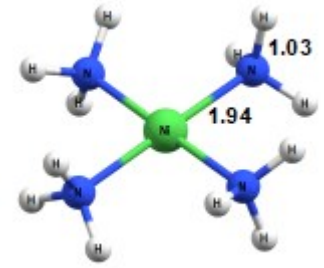
A	=	0.923436210 a.u. =	25.128 eV =	202670.8 cm**-1
B	=	0.005656900 a.u. =	0.154 eV =	1241.5 cm**-1
C	=	0.017691208 a.u. =	0.481 eV =	3882.8 cm**-1

C/B = 3.127

The ligand field one electron eigenfunctions:

Orbital	Energy (eV)	Energy(cm-1)	dxy	dyz	dz2	dxz	dx2-y2
1	0.000	0.0	-0.000000	-0.000000	-0.999998	-0.002048	0.000033
2	0.255	2059.9	-0.000000	-0.000000	0.002048	-0.999998	-0.000075
3	0.256	2062.4	-0.000430	-1.000000	0.000000	0.000000	-0.000000
4	0.799	6440.6	-1.000000	0.000430	0.000000	0.000000	0.000000
5	2.475	19959.3	0.000000	-0.000000	0.000033	-0.000075	1.000000

$[Ni(NH_3)_4]^{2+}$: 2S+1 = 1



Ni	0.000007000	0.000582000	0.000221000
N	1.370047000	1.370005000	0.012784000
H	1.640468000	1.630346000	-0.946262000
H	1.037923000	2.218747000	0.486983000
N	-1.370057000	1.369950000	-0.012615000
H	-2.213789000	1.042081000	-0.498623000
H	-1.640185000	1.630775000	0.946381000
N	1.369431000	-1.369662000	-0.016419000
H	1.630080000	-1.642615000	0.941802000
H	2.217992000	-1.036421000	-0.490206000
N	-1.369439000	-1.369643000	0.016335000
H	-1.041852000	-2.211889000	0.505184000
H	-1.629658000	-1.642657000	-0.941982000
H	1.041609000	-2.211941000	-0.505054000
H	2.213659000	1.042385000	0.499176000
H	-1.038107000	2.218452000	-0.487357000
H	-2.218210000	-1.036360000	0.489712000

AILFT (ORCA 4)

Racah Parameters :

A	=	0.904268340 a.u. =	24.606 eV =	198464.0 cm**-1
B	=	0.005629284 a.u. =	0.153 eV =	1235.5 cm**-1
C	=	0.021038208 a.u. =	0.572 eV =	4617.4 cm**-1

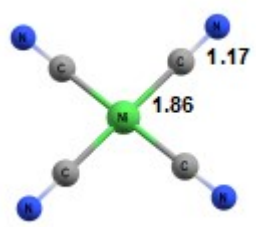
C/B = 3.737

The ligand field one electron eigenfunctions:

Orbital	Energy (eV)	Energy(cm-1)	dxy	dyz	dz2	dxz	dx2-y2
1	0.000	0.0	-0.000057	-0.075232	-0.000400	-0.997165	-0.001363
2	0.000	0.6	-0.001358	-0.997165	-0.000068	0.075232	0.000060

3	0.021	167.9	0.000000	-0.000098	1.000000	-0.000394	0.000038
4	0.380	3064.3	0.000007	-0.000043	-0.000038	-0.001363	0.999999
5	2.445	19721.5	-0.999999	0.001358	0.000000	-0.000046	0.000007

$[Ni(CN)_4]^{2-}$: 2S+1 = 1



Ni	0.000000000	0.000000000	0.000000000
C	1.860000000	0.000000000	0.000000000
C	-1.860000000	0.000000000	0.000000000
C	0.000000000	1.860000000	0.000000000
C	0.000000000	-1.860000000	0.000000000
N	3.033951000	0.000000000	0.000000000
N	-3.033951000	0.000000000	0.000000000
N	0.000000000	3.033951000	0.000000000
N	0.000000000	-3.033951000	0.000000000

AILFT (ORCA 4)

Racah Parameters :

A	=	0.878562169 a.u. =	23.907 eV =	192822.1 cm**-1
B	=	0.005620443 a.u. =	0.153 eV =	1233.5 cm**-1
C	=	0.015277010 a.u. =	0.416 eV =	3352.9 cm**-1

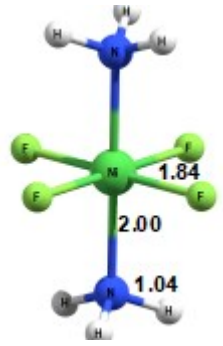
C/B = 2.718

The ligand field one electron eigenfunctions:

Orbital	Energy (eV)	Energy(cm-1)	dxy	dyz	dz2	dxz	dx2-y2
1	0.000	0.0	0.000005	-1.000000	-0.000000	0.000001	0.000000
2	0.000	1.6	-0.000000	-0.000001	0.000486	-1.000000	0.000011
3	0.086	693.5	0.000000	-0.000000	1.000000	0.000486	0.000014
4	0.121	978.8	-1.000000	-0.000005	0.000000	0.000000	0.000000
5	4.725	38106.7	0.000000	0.000000	-0.000014	0.000011	1.000000

S4: Geometrical structures and AI LFT d orbital energies for *trans*-$[NiL_4(NH_3)_2]$, L = F and CN

***trans*-$[NiF_4(NH_3)_2]$: 2S+1 = 3**



Ni	0.000000000	0.000000000	0.000000000
F	1.840000000	0.000000000	0.000000000
F	-1.840000000	0.000000000	0.000000000
F	0.000000000	1.840000000	0.000000000
F	0.000000000	-1.840000000	0.000000000
N	0.000000000	0.000000000	-2.000000000

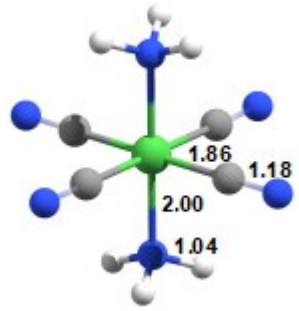
```
H        0.968583000     -0.008452000     -2.378649000
H       -0.491612000     -0.834591000     -2.378649000
H       -0.476971000      0.843044000     -2.378649000
N        0.000000000      0.000000000      2.000000000
H       -0.968583000     -0.008452000      2.378649000
H        0.491612000     -0.834591000      2.378649000
H        0.476971000      0.843044000      2.378649000
```

AILFT (ORCA 4)

```
Racah Parameters :
A               =  0.921206144 a.u. =    25.067 eV =  202181.4 cm**-1
B               =  0.005781433 a.u. =     0.157 eV =    1268.9 cm**-1
C               =  0.017312475 a.u. =     0.471 eV =    3799.6 cm**-1
C/B =  2.994

The ligand field one electron eigenfunctions:
Orbital    Energy (eV)  Energy(cm-1)      dxy        dyz        dz2        dxz        dx2-y2
    1          0.000        0.0         0.009076  -0.999959   0.000000   0.000013  -0.000000
    2          0.001       11.9         0.000000  -0.000013  -0.000122  -1.000000   0.000047
    3          0.305     2457.2        -0.999959  -0.009076  -0.000000  -0.000000   0.000000
    4          1.458    11756.5        -0.000000   0.000000   0.999997  -0.000122   0.002574
    5          1.800    14515.5         0.000000  -0.000000  -0.002574   0.000048   0.999997
```

***trans*-[Ni(CN)$_4$(NH$_3$)$_2$]: 2S+1 = 3**




```
Ni       0.000000000      0.000000000      0.000000000
C        1.857673000      0.000001000      0.000091000
C       -1.857673000     -0.000001000     -0.000091000
C        0.000001000      1.857893000      0.000000000
C       -0.000001000     -1.857892000      0.000000000
N        3.040481000      0.000002000     -0.000055000
N       -3.040482000     -0.000001000      0.000055000
N        0.000002000      3.040720000      0.000000000
N       -0.000002000     -3.040720000      0.000000000
N        0.000000000      0.000000000     -2.000000000
H        0.968583000     -0.008452000     -2.378649000
H       -0.491612000     -0.834591000     -2.378649000
H       -0.476971000      0.843044000     -2.378649000
N        0.000000000      0.000000000      2.000000000
H       -0.968583000     -0.008452000      2.378649000
H        0.491612000     -0.834591000      2.378649000
H        0.476971000      0.843044000      2.378649000
```

AILFT (ORCA 4)

```
Racah Parameters :
A               =  0.870125369 a.u. =    23.677 eV =  190970.4 cm**-1
B               =  0.006317027 a.u. =     0.172 eV =    1386.4 cm**-1
C               =  0.014076307 a.u. =     0.383 eV =    3089.4 cm**-1
C/B =  2.228

The ligand field one electron eigenfunctions:
Orbital    Energy (eV)  Energy(cm-1)      dxy        dyz        dz2        dxz        dx2-y2
    1          0.000        0.0         0.996640  -0.081909   0.000000  -0.000000  -0.000000
    2          0.125     1011.9        -0.000030  -0.000366   0.000822  -0.999936   0.011315
    3          0.126     1015.1        -0.081909  -0.996640  -0.000000   0.000367  -0.000004
    4          2.661    21462.7        -0.000000   0.000000   1.000000   0.000828   0.000457
    5          4.077    32882.8         0.000000  -0.000000  -0.000466   0.011314   0.999936
```