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ARTICLE

A theoretical modeling of the L$_{2,3}$-edge X-ray absorption spectra of Mn(acac)$_2$ and Co(acac)$_2$ complexes.

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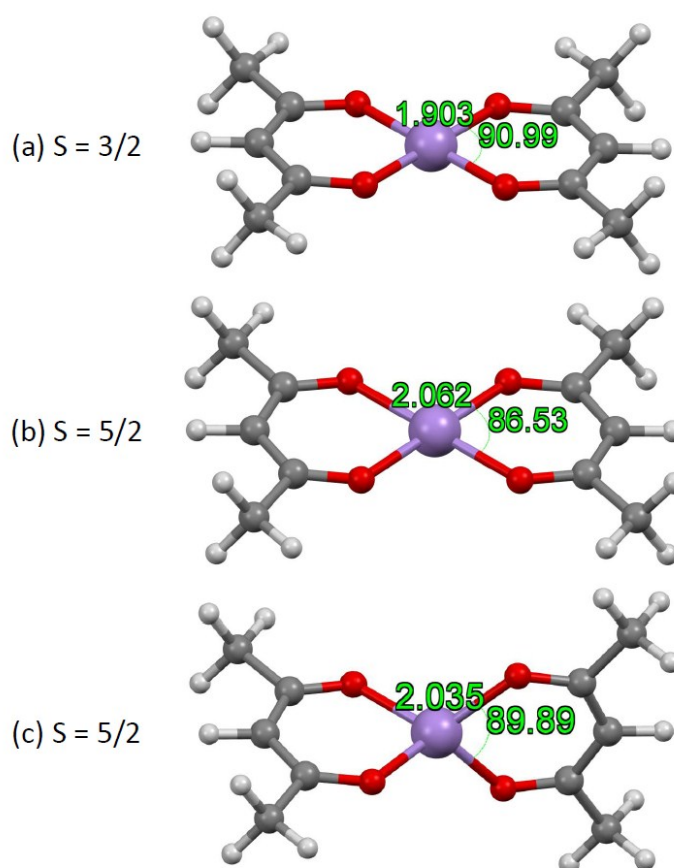
Figure S1. B3LYP Optimized geometries for **I** with a square planar (a) and (b), and a distorted tetrahedral (c) arrangement. Bond lengths are in Å and bond angles are in deg.

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Table S1 Optimized Cartesian Coordinates for **I** in the S=5/2 (HS) tetrahedral distorted structure.

```
Mn       0.000      0.000       0.000
O        1.017     -1.017      -1.441
O       -1.017      1.017      -1.441
O        1.017      1.017       1.441
O       -1.017     -1.017       1.441
C        1.766     -1.766      -3.554
C       -1.766      1.766      -3.554
C        0.884     -0.884      -2.699
C       -0.884      0.884      -2.699
C        0.000      0.000      -3.337
C        0.000      0.000       3.337
C        0.884      0.884       2.699
C       -0.884     -0.884       2.699
C        1.766      1.766       3.554
C       -1.766     -1.766       3.554
H        2.405     -1.160      -4.201
H        1.160     -2.405      -4.201
H        2.389     -2.389      -2.916
H       -1.160      2.405      -4.201
H       -2.405      1.160      -4.201
H       -2.389      2.389      -2.916
H        0.000      0.000      -4.420
H        0.000      0.000       4.420
H        2.405      1.160       4.201
H        1.160      2.405       4.201
H        2.389      2.389       2.916
H       -1.160     -2.405       4.201
H       -2.397     -1.160       4.201
H       -2.389     -2.389       2.916
```

Table S2 Optimized Cartesian Coordinates for **I** in the S=5/2 (HS) square planar structure.

```
Mn      0.000     0.000     0.000
O       1.413     1.501     0.001
O       1.413    -1.501    -0.001
O      -1.413     1.501    -0.001
O      -1.413    -1.501     0.001
C       1.244     2.762     0.001
C       1.244    -2.762    -0.001
C      -1.244     2.762    -0.001
C      -1.244    -2.762     0.001
C       0.000     3.409     0.000
C       0.000    -3.409     0.000
C       2.496     3.610     0.002
C       2.496    -3.610    -0.002
C      -2.496     3.610    -0.002
C      -2.496    -3.610     0.002
H       0.000     4.491     0.000
H       0.000    -4.491     0.000
H       3.375     2.969     0.002
H       3.375    -2.969    -0.002
H      -3.375     2.969    -0.002
H      -3.375    -2.969     0.002
H       2.520     4.257     0.882
H       2.521     4.257    -0.878
H      -2.521     4.257     0.878
H      -2.520     4.257    -0.882
H       2.521    -4.257     0.878
H       2.520    -4.257    -0.882
H      -2.520    -4.257     0.882
H      -2.521    -4.257    -0.878
```
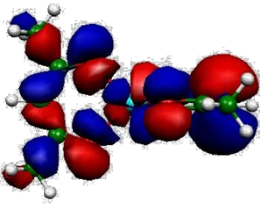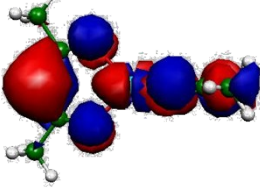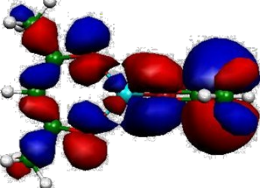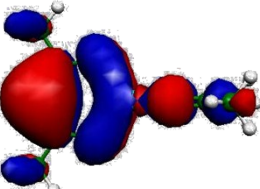
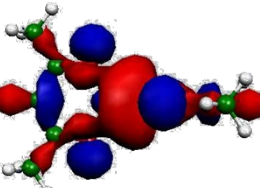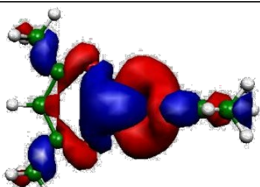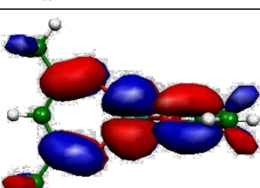**Table S3** Optimized Cartesian Coordinates for **I** in the S=3/2 square planar structure.

```
Mn     0.000     0.000     0.001
O      1.357     1.334     0.001
O      1.357    -1.334     0.000
O     -1.357     1.334     0.000
O     -1.357    -1.334     0.001
C      1.229     2.609     0.001
C      1.229    -2.609     0.000
C     -1.229     2.609     0.000
C     -1.229    -2.609     0.001
C      0.000     3.271     0.000
C      0.000    -3.271     0.000
C      2.512     3.402     0.001
C      2.512    -3.402    -0.001
C     -2.512     3.402    -0.001
C     -2.512    -3.402     0.001
H      0.000     4.353     0.000
H      0.000    -4.353     0.000
H      3.364     2.725     0.001
H      3.364    -2.725    -0.001
H     -3.364     2.725    -0.001
H     -3.364    -2.725     0.001
H      2.568     4.047     0.881
H      2.568     4.047    -0.879
H     -2.568     4.047     0.879
H     -2.567     4.047    -0.881
H      2.568    -4.047     0.879
H      2.567    -4.047    -0.881
H     -2.567    -4.047     0.881
H     -2.568    -4.047    -0.879
```

Table S4 Optimized Cartesian Coordinates for **II** in the S=3/2 (HS) tetrahedral distorted structure.

```
Co     0.000     0.000     0.000
O      1.023    -1.023    -1.308
O     -1.023     1.023    -1.308
O      1.023     1.023     1.308
O     -1.023    -1.023     1.308
C      1.762    -1.762    -3.429
C     -1.762     1.762    -3.429
C      0.885    -0.885    -2.568
C     -0.885     0.885    -2.568
C      0.000     0.000    -3.200
C      0.000     0.000     3.200
C      0.885     0.885     2.568
C     -0.885    -0.885     2.568
C      1.762     1.762     3.429
C     -1.762    -1.762     3.429
H      2.397    -1.153    -4.076
H      1.153    -2.397    -4.076
H      2.389    -2.389    -2.798
H     -1.153     2.397    -4.076
H     -2.397     1.153    -4.076
H     -2.389     2.389    -2.798
H      0.000     0.000    -4.282
H      0.000     0.000     4.282
H      2.397     1.153     4.076
H      1.153     2.397     4.076
H      2.389     2.389     2.798
H     -1.153    -2.397     4.076
H     -2.397    -1.153     4.076
H     -2.389    -2.389     2.798
```

Table S5. Energy (eV) , d-composition and MOs for **I**. Symmetry in parenthesis.

	Energy (eV)	d-composition	MOs
HOMO (e)	-5.6375	25.4% d_{xz} 25.4% d_{yz}	
HOMO-1 (e)	-6.4649	3.7% d_{yz} + 3.6% d_{xz} 3.7% d_{xz} + 3.6% d_{yz}	
HOMO-2 (a$_1$)	-6.9718	58.2% d_{z2}	
HOMO-3 (b$_2$)	-7.5026	76.9% d_{xy}	
HOMO-4 (b$_1$)	-7.7019	81.6% d_{x2-y2}	
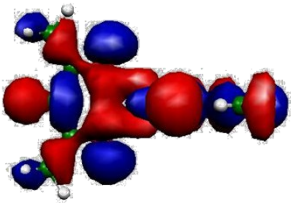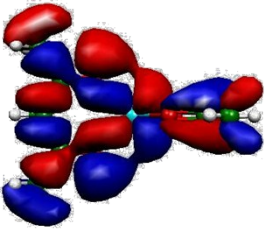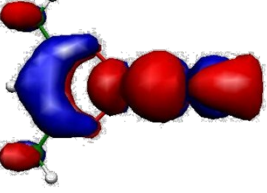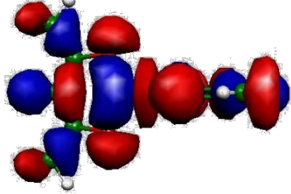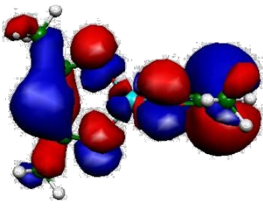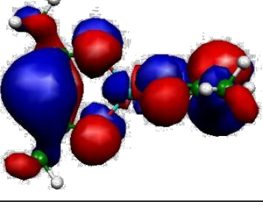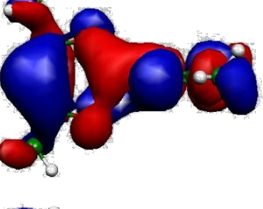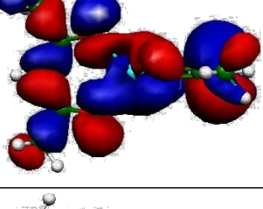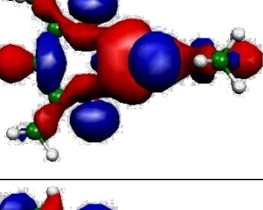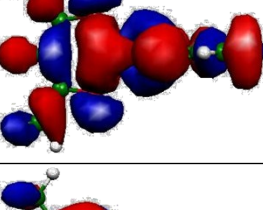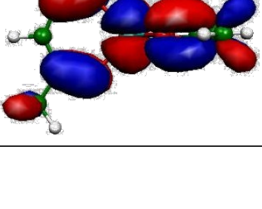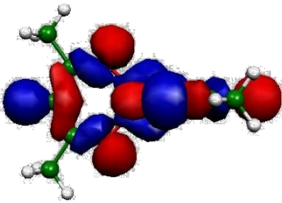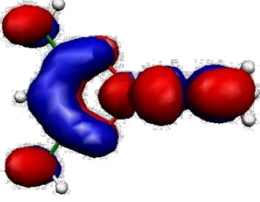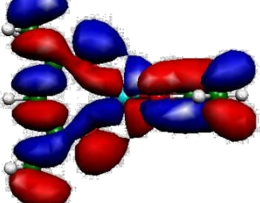
HOMO-5 (a₁)	-8.1900	11 % d_{xy}	
HOMO-6 (e)	-8.3462	21.7% d_{yz} + 20.6% d_{xz}	
		21.7% d_{xz} + 20.6% d_{yz}	
HOMO-7 (a₁)	-9.0594	37.8% d_{z2}	

Table S6. Energy (eV) , d-composition and MOs for **II**. Symmetry in parenthesis.

	Energy (eV)	d-composition	MOs
HOMO (e)	-6.1025	$11.3\%\ d_{yz} + 0.6\%\ d_{xz}$ $11.3\%\ d_{xz} + 0.6\%\ d_{yz}$	
HOMO-1 (e)	-6.7317	$9\%\ d_{yz} + 2.2\%\ d_{xz}$ $9\%\ d_{xz} + 2.2\%\ d_{yz}$	
HOMO-2 (a_1)	-7.4872	$50.1\%\ d_{z2}$	
HOMO-3 (a_1)	-8.1070	$10.2\%\ d_{xy}$	
HOMO-4 (b_1)	-8.1655	$73\%\ d_{x2-y2}$	

HOMO-5 (b_2)	-9.0431	61.3% d_{xy}	
HOMO-6 (e)	-9.2354	25.7% d_{yz} + 19.4% d_{xz}	
		25.7% d_{xz} + 19.4% d_{yz}	
HOMO-7 (a_1)	-9.3752	45% d_{z2}	

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