On the mechanism of the photoinduced magnetism in copper octacyanomolybdates

Supporting Information

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S1. Computational Details

Geometry optimization has been carried out using DFT methods, since they are known to yield very reliable results, in order to obtain the optimal geometry for each of the electronic states considered for the metallic centers:

a) [Cu(CNH)(tris(2-aminoethyl)amine)]$^{2+/1+}$: Cu TZV[1] and SV[2] basis set for N, C, H.

Other basis sets and functionals were used for testing purposes and the results did not vary significantly. Specifically, the functional B3LYP and the following basis sets: Los Alamos ECP LanL2dz for Mo and D95V[3] for C, N and H, Cu: TZV, N: DZV, C and H SV.

b) $[Mo(CNH)_4(CN)_2]^{2+/3+}$: LanL2DZ ECP for Mo and SV basis set for N, C, H. Other basis sets were used for testing purposes and the results did not vary significantly. Specifically, Los Alamos ECP LanL2DZ for Mo and D95V for C, N and H, Stuttgart SDD ECP for Mo, and SV for N, C, H, and SDD ECP for Mo, and TZV for N, C, H.

The objective of the ONIOM calculations was to check the reliability of the changes in the coordination sphere of Mo for the different electronic states considered, obtained by optimization of the model $[Mo(CNH)_6(CN)_2]^{2+}$, compared with the behavior of the $[Mo(CN)_2(CN\text{-}Cu(tris(2\text{-}aminoethyl)amine)_6]^{8+}$ molecule. For this reason only the Mo and the eight CN coordinated to the metal were included in the QM part. The Cu atoms and the tris(2-aminoethyl)amine ligand were left in the MM part. The high level method used was UB3LYP and the basis set LanL2DZ for Mo and D95V for C, N and H, and the UFF force field was used for the MM calculation. To check the formation of seven-coordinated complexes found by optimization of some $[Mo(CNH)_6(CN)_2]^{2+}$ models, one of the Cu(CN)(CuCNL) and one CN- ligand were also included in the QM region, in order to describe properly the hydrogen bond formation, which is probably related to the decoordination process.

Full DFT optimization of the whole $[Mo(CN)_2(CN\text{-}Cu(tris(2\text{-}aminoethyl)amine)_6]^{8+}$ molecule was attempted but SCF convergence problems forced us to abandon.

The optimization of the dimers in the quartet state was done with the BP86 functional and the same basis set for the two metals (LanL2DZ ECP for Mo and Cu) and SV basis set for N, C and H. The six possible dimers were optimized. The initial geometry was generated by superimposition of the optimized [Cu(CNH)(tris(2-aminoethyl)amine)]$^{2+}$ and $[Mo(CNH)_6(CN)_2]^{2+}$ models in all the possible positions, as it is shown in Figure S1. All the possibilities were calculated and the results do not change substantially from one dimer to the other. For this reason, and to avoid reporting meaningless data, only results for one of the dimers are shown.

Finally, full optimization of whole the molecule for S=4 was carried out, in order to check the reliability of the ligand dissociation obtained in the model dimers and by ONIOM. The basis set used was the Ahlrichs double zeta plus polarization basis set[2] and the relativistic effects were introduced by the ZORA formalism[5].

The ONIOM and the DFT geometry optimizations for the dimers were done with Gaussian03 suite of programs.[6] The DFT optimization of the whole molecule was one with ORCA.[7]

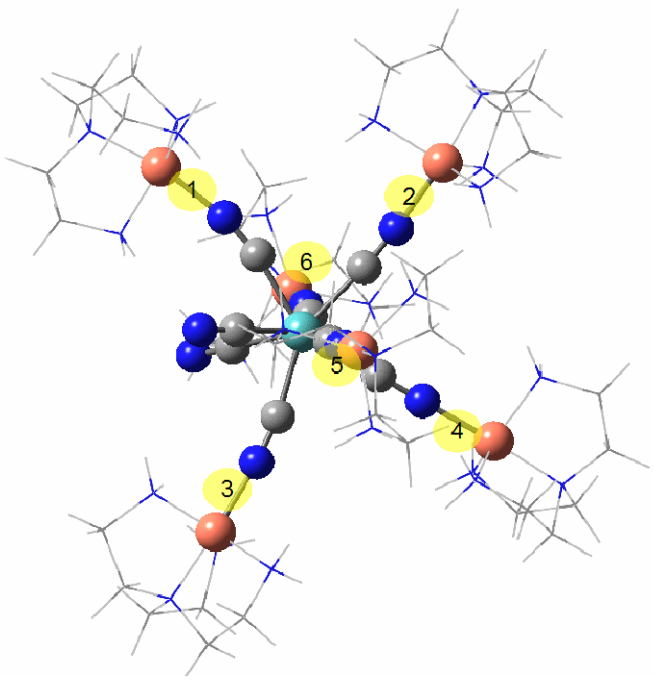

Figure S1. The six possible dimers on the initial structure.

To compute the energy of the excited states, accurate electronic structure calculations were performed using SA-CASSCF and CASPT2 techniques with the MOLCAS package.[8] A CAS(3,3) was used to have a general picture of the main states involved in the photomagnetic process and five states were averaged. In this way it is possible to map the energy of all the relevant states potentially involved in the process: from the ground state $Mo^{IV,CS}$ till the charge transfer state. This CAS includes the dz^2 orbital of Cu, and the dz^2 and dxy orbitals of Mo. However, consistency of these results were checked by using a larger CAS(11,12) including the 3d orbitals plus the polarization d shell for the Cu (so 10 orbitals to describe the Cu) and two d orbitals for Mo. To accelerate the CASPT2 calculations, Cu, Mo and first neighboring atoms (C and N) were selected for defining the correlation orbital space (active sites) in the CASPT2 calculation, and inactive orbitals with less than 0.1 of the density on the active sites were frozen, and no virtual orbitals were deleted.

The ANO-RCC basis set was used and the contraction applied is shown in Table S1.

Table S1. Basis set used in the CAS(3,3) calculations for the model dimers.

Atom	Contraction	reference
Mo	21s18p13d6f4g2h/7s6p4d2f	9
Cu	21s15p10d6f4g2h/6s5p3d2f	9
N coordinated to Cu	14s9p4d3f2g/4s3p1d	10
N non coordinated to Cu	14s9p4d3f2g/3s2p	10
C coordinated to Mo	14s9p4d3f2g/4s3p1d	10
C non coordinated to Mo	14s9p4d3f2g/3s2p	10
H	8s4p3d1f/2s	11

However, to obtain an accurate value of the energetic splitting between the quartet and triplet state, which has a very small magnitude, it is necessary to improve the description of the electronic dynamic correlation. Since variational methods are not applicable at present to such a large system (even to the model dimers), an extended CASSCF-CASPT2 was used (3 electrons in 11 orbitals, including a double shell Mo d orbitals plus the Cu dz^2 singly occupied orbital), and a contraction which allows more flexibility to describe the Mo and Cu centers (shown in Table S2). Only one doublet and one quartet states were computed, to have the best orbitals for the states of interest.

Table S2. Basis set used to compute the doublet-quartet energy splitting for the seven-coordinated Mo complexes.

Atom	Contraction	reference
Mo	21s18p13d6f4g2h/ 7s6p5d6f4g2h	9
Cu	21s15p10d6f4g2h/ 6s5p4d6f4g2h	9
N coordinated to Cu	14s9p4d3f2g/4s3p1d	10
N non coordinated to Cu	14s9p4d3f2g/3s2p	10
C coordinated to Mo	14s9p4d3f2g/4s3p1d	10
C non coordinated to Mo	14s9p4d3f2g/3s2p	10
H	8s4p3d1f/2s	11

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S2. Cartesian coordinates

A. Optimized $[Mo(CNH)_4(CN)_2]^{2+}$ (Mo^{IV} closed shell)

42	-1.686021	12.100284	15.166210
7	-1.630327	12.327604	18.483374
7	-3.371370	9.457334	16.344601
7	-4.787977	13.261872	14.882596
7	-2.602138	10.571707	12.330773
7	-0.466675	13.917581	12.661560
7	0.701742	9.794397	14.988670
7	1.341981	13.193244	16.076123

7	-2.016260	15.329673	15.974711
6	-1.676086	12.205172	17.310843
6	-1.895288	14.176797	15.687283
6	-2.777877	10.387871	15.926901
6	-3.679273	12.861618	14.988260
6	-2.280415	11.108621	13.331161
6	-0.918990	13.242336	13.516726
6	-0.138021	10.625526	15.057281
6	0.259738	12.806274	15.751492
1	1.503702	9.160353	14.970704
1	-5.703077	13.714700	14.827591
1	-2.871044	10.122647	11.450398
1	-3.881949	8.656983	16.728979
1	-1.540487	12.511102	19.485911
1	-0.042423	14.559555	11.987203

B. Optimized $[Mo(CNH)_4(CN)_2]^{2+}$ (Mo^{IV} triplet)

42	-1.658284	12.144425	15.183015
7	-1.943625	13.504037	18.207420
7	-2.549570	9.521867	17.216167
7	-5.143978	12.161477	15.207453
7	-2.676095	11.706703	11.930114
7	0.550387	13.868039	13.385568
7	0.093984	9.349728	14.056499
7	1.258886	11.959632	16.720312
7	-2.765553	15.232362	14.799979
6	-1.826572	12.984715	17.154016
6	-2.365531	14.114299	14.983902
6	-2.353250	10.442921	16.501386
6	-3.969481	12.097738	15.086652
6	-2.260985	11.765446	13.035558
6	-0.264885	13.268944	13.993384
6	-0.578659	10.217841	14.494664
6	0.217439	12.049319	16.127615
1	0.713204	8.611307	13.712062
1	-6.157331	12.266242	15.304674
1	-3.044419	11.676725	10.975543
1	-2.698212	8.724981	17.841171
1	-1.998742	13.997096	19.101855
1	1.262736	14.427407	12.910345

C. Optimized $[Mo(CNH)_4(CN)_2]^{2+}$ (Mo^{IV} open shell singlet). It was obtained by optimizing first the triplet state and in a second step, the open shell singlet by reading the previously computed triplet orbitals and geometry.

42	-1.720438	12.045556	15.144041
7	-1.772467	14.011905	17.823733
7	-2.446290	9.515344	17.184067
7	-5.029288	11.893950	15.503201
7	-2.744352	11.769412	11.987111
7	0.751093	13.956005	14.006776
7	-0.082445	9.519176	13.718285
7	0.991823	11.349556	16.975947

7	-3.039860	14.971765	14.199203
6	-1.772482	13.299133	16.883901
6	-2.575417	13.923720	14.531385
6	-2.221096	10.406253	16.442294
6	-3.856289	11.912027	15.369426
6	-2.376431	11.829735	13.107661
6	-0.125247	13.264442	14.387699
6	-0.694172	10.400760	14.211001
6	0.022250	11.589357	16.322588
1	0.480810	8.754993	13.336608
1	-6.047830	11.928243	15.594356
1	-3.065716	11.770556	11.015775
1	-2.597071	8.756819	17.853898
1	-1.743266	14.647331	18.624425
1	1.505645	14.577213	13.705972

D. Optimized [Cu(CNH)(tris(2-aminoethyl)amine)]$^{2+}$

6	3.820679	-0.002960	0.000226
7	2.643963	-0.002588	0.000030
29	0.658325	-0.000176	0.001120
7	-1.427189	0.002976	-0.002735
6	-1.861224	1.276962	-0.708064
6	-0.925152	2.437284	-0.359228
7	0.494590	2.004460	-0.620837
7	0.484422	-0.465994	2.047665
6	-0.937007	-0.905480	2.286446
6	-1.868412	-0.022387	1.451473
7	0.485988	-1.548379	-1.419892
6	-0.932436	-1.529280	-1.928670
6	-1.868352	-1.242561	-0.751770
1	1.158215	-1.199496	2.340542
1	0.714366	0.380137	2.607343
1	1.165200	-1.443752	-2.198020
1	0.706586	-2.455136	-0.960544
1	1.172095	2.622881	-0.134666
1	0.721876	2.062719	-1.634194
1	-1.219761	-0.847784	3.363002
1	-1.017072	-1.976150	1.995877
1	-2.925349	-0.374637	1.517738
1	-1.852479	1.022847	1.833436
1	-1.216663	-2.489468	-2.417968
1	-1.004386	-0.742010	-2.711427
1	-2.923680	-1.121853	-1.094555
1	-1.856800	-2.093913	-0.035228
1	-1.004530	2.719999	0.714001
1	-1.203669	3.342960	-0.946236
1	-2.918043	1.515802	-0.439297
1	-1.844216	1.083103	-1.804302
1	4.915887	-0.003927	-0.000091

E. Optimized [Cu(CNH)(tris(2-aminoethyl)amine)]$^{1+}$

6	-4.040661	0.002963	-0.002205

7	-2.850032	0.001573	-0.000274
29	-0.975225	0.002083	-0.001052
7	1.835428	0.002549	-0.002858
6	2.081976	-0.960971	-1.087717
6	0.962621	-2.010223	-1.248346
7	-0.367897	-1.369832	-1.493648
7	-0.362650	-0.629129	1.924285
6	0.960573	-0.082642	2.361903
6	2.085841	-0.453744	1.373877
7	-0.365493	1.981531	-0.418118
6	0.957024	2.091689	-1.110631
6	2.083605	1.423306	-0.296295
1	-1.113579	-0.330138	2.573417
1	-0.349301	-1.667411	1.938969
1	-1.117640	2.393565	-1.000600
1	-0.353074	2.511880	0.474757
1	-1.115130	-2.087072	-1.534850
1	-0.372692	-0.878669	-2.408549
1	1.247407	-0.443185	3.381231
1	0.858488	1.024748	2.431237
1	3.053137	-0.056274	1.783729
1	2.199489	-1.563721	1.357874
1	1.241228	3.155743	-1.305883
1	0.855367	1.599664	-2.105101
1	3.050548	1.580789	-0.846037
1	2.197415	1.964475	0.673152
1	0.873814	-2.621473	-0.321109
1	1.248033	-2.713295	-2.070201
1	3.054468	-1.508133	-0.957631
1	2.181771	-0.391932	-2.042466
1	-5.129607	0.000922	-0.000663

F. ONIOM optimized structure for the $[Mo(CuNL)_4(CN)_2]^{8+}$ (Mo^{IV} closed shell singlet)

42	10421006	8.661369	4.542385	14.502682
29	10291003	7.296955	7.012417	10.054323
29	10291003	10.279138	0.511650	11.512429
29	10291003	12.943873	7.003204	12.587515
29	10291003	12.602846	2.476219	17.389465
29	10291003	9.419940	8.506375	17.892823
29	10291003	5.982437	2.031311	18.279192
7	10071001	7.842029	6.124668	11.702054
7	10071001	9.726123	2.002290	12.638864
7	10071001	11.405892	6.035978	13.294237
7	10071001	11.115206	3.228821	16.377480
7	10071001	9.161015	7.051256	16.623393
7	10071001	7.076574	2.921185	16.931904
7	10071001	5.890237	6.287980	15.109244
7	10071001	6.171022	2.788306	13.155669
7	10071003	6.762221	7.924818	8.389512
7	10071003	6.102842	8.225615	11.043565
1	10011000	5.568355	7.708637	11.778879
1	10011000	6.667353	8.987375	11.485293

7	10071003	6.589750	5.334021	9.307830
1	10011000	7.231141	4.533226	9.510661
1	10011000	5.644010	5.142635	9.711539
7	10071003	9.157360	7.540855	9.680989
1	10011000	9.641021	7.860499	10.551180
1	10011000	9.671481	6.729893	9.266459
7	10071003	9.392123	1.299641	9.941130
1	10011000	8.365925	1.101540	9.983018
1	10011000	9.552015	2.332252	9.897551
7	10071003	9.309648	-0.776712	12.641646
1	10011000	8.371382	-0.404456	12.914954
7	10071003	14.487275	8.001170	11.872346
7	10071003	12.062947	8.728603	12.942278
1	10011000	11.370538	8.930655	12.184897
1	10011000	11.580227	8.719401	13.869464
7	10071003	12.749300	6.138908	10.830106
1	10011000	13.174558	5.183752	10.860864
1	10011000	11.743598	6.069664	10.553988
7	10071003	14.139147	6.210498	13.935468
1	10011000	14.020068	6.710833	14.846311
1	10011000	13.940070	5.191480	14.060619
7	10071003	14.125154	1.716616	18.385794
7	10071003	13.037560	1.257887	15.903869
1	10011000	12.170490	0.837141	15.497801
1	10011000	13.556867	1.783430	15.163376
7	10071003	11.411791	1.877930	18.836526
1	10011000	10.707299	2.615396	19.067018
1	10011000	10.926175	0.997112	18.549446
7	10071003	13.469371	4.240372	17.511007
1	10011000	13.391730	4.760908	16.607708
1	10011000	13.025364	4.795174	18.278570
7	10071003	9.689278	9.973186	19.183141
7	10071003	10.094186	9.695574	16.475995
1	10011000	11.093736	9.463133	16.273718
1	10011000	9.524358	9.603664	15.603993
7	10071003	10.683705	7.419975	18.942357
1	10011000	10.152508	6.751426	19.546467
1	10011000	11.333517	6.891513	18.316150
7	10071003	7.506803	8.513834	18.357664
1	10011000	6.970555	9.027480	17.621015
1	10011000	7.138676	7.539247	18.449692
7	10071003	4.879451	1.129298	19.642564
7	10071003	5.502577	3.754647	19.102044
1	10011000	6.291268	4.085570	19.704177
1	10011000	5.289042	4.472588	18.372210
7	10071003	7.537569	1.024576	18.945657
1	10011000	7.731228	0.217148	18.309577
1	10011000	8.380514	1.639433	19.005386
7	10071003	4.822850	1.247595	16.894291
1	10011000	4.139491	1.966928	16.563121
1	10011000	5.387342	0.896931	16.086848
6	10061001	8.150590	5.579178	12.691326

6	10061001	9.350724	2.895363	13.301373
6	10061001	10.458624	5.488066	13.713774
6	10061001	10.240511	3.683110	15.744270
6	10061001	8.964949	6.177282	15.864800
6	10061001	7.681124	3.472137	16.093839
6	10061001	6.867817	5.653953	14.885734
6	10061001	7.045325	3.427298	13.640090
6	10061003	5.182025	8.792201	10.067224
1	10011000	4.366438	8.066038	9.860703
1	10011000	4.721887	9.722694	10.467182
6	10061003	5.941155	9.094853	8.776663
1	10011000	5.229305	9.378311	7.968618
1	10011000	6.577255	9.986504	8.972443
6	10061003	6.484710	5.533242	7.868328
1	10011000	5.786814	4.787965	7.426771
1	10011000	7.482474	5.390518	7.399890
6	10061003	5.983957	6.950147	7.590870
1	10011000	4.905494	6.975454	7.863156
1	10011000	6.045850	7.174005	6.501770
6	10061003	9.097301	8.631509	8.718103
1	10011000	10.078980	8.748321	8.207811
1	10011000	8.868220	9.581828	9.246957
6	10061003	8.003897	8.334713	7.693992
1	10011000	8.383875	7.522706	7.035007
1	10011000	7.833308	9.222990	7.044395
6	10061003	9.974723	0.657879	8.770240
1	10011000	9.306102	0.783565	7.890091
1	10011000	10.950329	1.134273	8.532571
6	10061003	10.184725	-0.826978	9.062577
1	10011000	9.180825	-1.306619	9.058932
6	10061003	13.110252	9.740264	12.938961
1	10011000	13.636037	9.733913	13.918185
1	10011000	12.668871	10.750569	12.790661
6	10061003	14.101019	9.429887	11.819243
1	10011000	14.990169	10.095904	11.895889
1	10011000	13.596539	9.675684	10.858334
6	10061003	13.469985	6.973625	9.878864
1	10011000	12.839782	7.845397	9.598730
1	10011000	13.693738	6.397584	8.953950
6	10061003	14.767755	7.460217	10.522371
1	10011000	15.258719	8.219551	9.872510
1	10011000	15.455873	6.587327	10.572960
6	10061003	15.497661	6.392971	13.442170
1	10011000	15.727579	5.609007	12.688569
1	10011000	16.226230	6.293278	14.276941
6	10061003	15.619311	7.774571	12.800345
1	10011000	16.598765	7.872225	12.279608
1	10011000	15.618731	8.520090	13.626280
6	10061003	14.857588	0.825008	17.457611
1	10011000	15.617786	1.389038	16.872819
6	10061003	12.259852	1.624399	19.993917
1	10011000	11.734134	0.963418	20.718012

1	10011000	12.485918	2.584489	20.506138
6	10061003	13.561326	0.968495	19.533036
1	10011000	13.317150	-0.079339	19.249925
1	10011000	14.284571	0.913163	20.377917
6	10061003	14.870544	3.994972	17.823265
1	10011000	15.338070	4.913799	18.241209
1	10011000	15.416006	3.722981	16.893769
6	10061003	14.966318	2.851207	18.831478
1	10011000	16.028223	2.543734	18.965198
1	10011000	14.620915	3.248626	19.811622
6	10061003	9.997197	11.054330	16.991869
1	10011000	8.953097	11.419413	16.883092
1	10011000	10.662136	11.733454	16.413710
6	10061003	10.394231	11.061231	18.467085
1	10011000	11.497473	10.923453	18.509796
1	10011000	10.176393	12.055075	18.919773
6	10061003	11.440973	8.346371	19.773018
1	10011000	12.251542	8.808881	19.169497
1	10011000	11.910816	7.804600	20.623468
6	10061003	10.503678	9.433264	20.295939
1	10011000	9.861886	8.965304	21.075045
1	10011000	11.088151	10.235998	20.799918
6	10061003	7.391381	9.209742	19.632332
1	10011000	6.346213	9.557655	19.787411
1	10011000	7.649207	8.514205	20.460030
6	10061003	8.348281	10.400690	19.643752
1	10011000	7.917609	11.173347	18.968892
1	10011000	8.391247	10.850335	20.661624
6	10061003	4.321483	3.511969	19.919683
1	10011000	3.417209	3.506548	19.273652
1	10011000	4.201943	4.321936	20.672797
6	10061003	4.462519	2.161246	20.619455
1	10011000	3.506986	1.885510	21.120383
1	10011000	5.222149	2.286260	21.422665
6	10061003	7.185349	0.538808	20.272972
1	10011000	7.327007	1.352736	21.016488
1	10011000	7.846299	-0.308670	20.560200
6	10061003	5.725393	0.089734	20.272586
1	10011000	5.677205	-0.866891	19.706536
1	10011000	5.390959	-0.133575	21.311041
6	10061003	3.716613	0.537422	18.942168
1	10011000	2.882323	1.268547	18.856896
6	10061003	4.113498	0.140376	17.521428
1	10011000	4.773204	-0.753526	17.552609
1	10011000	3.207841	-0.120352	16.930385
1	10011000	3.316327	-0.345044	19.490904
1	10011000	15.402629	0.024281	18.006980
6	10061003	13.884999	0.209068	16.454201
1	10011000	14.446516	-0.298803	15.639052
1	10011000	13.253159	-0.551083	16.962303
1	10011000	9.873158	-0.982944	13.498434
1	10011000	10.770836	-1.301477	8.243211

7	10071003	12.177457	0.898681	11.866955
1	10011000	12.331173	1.132902	12.874122
1	10011000	12.489360	1.696526	11.266656
7	10071003	10.853796	-0.992238	10.373471
6	10061003	12.327314	-0.911129	10.249893
1	10011000	12.775774	-1.911608	10.054931
1	10011000	12.625203	-0.254382	9.402565
6	10061003	10.429893	-2.239051	11.050976
1	10011000	10.273180	-3.065915	10.321723
1	10011000	11.201733	-2.588488	11.772136
6	10061003	9.150824	-1.988063	11.847953
1	10011000	8.936348	-2.856169	12.509672
1	10011000	8.293506	-1.866000	11.151271
6	10061003	12.921165	-0.304333	11.519502
1	10011000	13.994925	-0.060529	11.361077
1	10011000	12.853578	-1.036587	12.352980

G. ONIOM optimized structure for the $[Mo(CuNL)_6(CN)_2]^{8+}$ (Mo^{IV} triplet)

42	10421006	8.883384	4.546790	14.487136
29	10291003	6.650892	7.161816	10.395930
29	10291003	11.360469	0.340169	12.382493
29	10291003	12.473669	7.025520	11.463532
29	10291003	11.503927	2.248250	18.532856
29	10291003	10.557749	8.255300	17.904045
29	10291003	4.598776	2.510655	16.857571
7	10071001	7.470276	6.213855	11.862677
7	10071001	10.430602	1.851885	13.135008
7	10071001	11.122533	6.134139	12.514521
7	10071001	10.570158	3.042856	17.044826
7	10071001	9.900409	6.937844	16.659315
7	10071001	6.132330	3.257408	15.960053
7	10071001	6.649950	6.485114	16.076815
7	10071001	7.112659	2.073671	13.064442
7	10071003	5.858386	8.150656	8.881888
7	10071003	7.260934	8.888234	11.125706
1	10011000	7.118655	8.928725	12.160920
1	10011000	8.272209	9.029662	10.902909
7	10071003	4.855877	6.497682	10.849287
1	10011000	4.885038	5.486584	11.114490
1	10011000	4.461528	7.061594	11.637011
7	10071003	7.742991	6.165677	9.095112
1	10011000	8.715920	6.021063	9.446000
1	10011000	7.297508	5.238625	8.904747
7	10071003	12.713806	1.515049	11.566449
1	10011000	12.327422	1.938757	10.691652
1	10011000	13.001657	2.270189	12.230044
7	10071003	9.770611	-0.194206	11.351197
1	10011000	9.304280	0.637762	10.922311
7	10071003	13.863599	7.963175	10.423106
7	10071003	11.178288	7.494936	10.060208
1	10011000	11.040771	6.672665	9.429048
1	10011000	10.264726	7.786421	10.474204

7	10071003	13.522361	5.369680	11.286373
1	10011000	14.049909	5.190927	12.171672
1	10011000	12.899998	4.557419	11.072573
7	10071003	12.833398	8.269519	12.948853
1	10011000	12.097598	9.012719	12.969144
1	10011000	12.850397	7.762237	13.862948
7	10071003	12.450858	1.471936	20.080478
7	10071003	11.227935	0.426562	17.843375
1	10011000	10.264196	0.311003	17.454351
1	10011000	11.938629	0.223590	17.103953
7	10071003	10.203748	3.023933	19.793780
1	10011000	9.945551	3.998985	19.519694
1	10011000	9.345231	2.426811	19.820854
7	10071003	13.156153	3.218759	18.076833
1	10011000	13.331099	3.197691	17.046062
1	10011000	13.083961	4.209318	18.403666
7	10071003	11.268515	9.579629	19.180790
7	10071003	11.894372	8.877113	16.597889
1	10011000	12.694262	8.203757	16.567779
1	10011000	11.469846	8.967324	15.646674
7	10071003	11.009608	6.845541	19.203476
1	10011000	10.146669	6.560138	19.720999
1	10011000	11.427322	6.014841	18.726159
7	10071003	8.809514	9.151577	18.009424
1	10011000	8.679731	9.764831	17.172120
1	10011000	8.032581	8.453802	18.063194
7	10071003	3.033456	1.751657	17.786296
7	10071003	3.667485	4.245172	16.812888
1	10011000	4.041556	4.861372	17.570833
1	10011000	3.788119	4.712225	15.885020
7	10071003	5.696638	2.021604	18.418275
1	10011000	6.222732	1.141204	18.212715
1	10011000	6.367909	2.786091	18.660664
7	10071003	4.313428	1.205250	15.411644
1	10011000	3.834277	1.673072	14.608144
1	10011000	5.220566	0.794063	15.093098
6	10061001	7.958921	5.649075	12.746064
6	10061001	9.880130	2.762869	13.591137
6	10061001	10.337972	5.596705	13.173512
6	10061001	10.002552	3.542463	16.170197
6	10061001	9.526118	6.131250	15.917391
6	10061001	7.064013	3.708204	15.434434
6	10061001	7.425771	5.804957	15.542407
6	10061001	7.727799	2.918692	13.572044
6	10061003	6.465989	9.921802	10.477495
1	10011000	5.472740	9.991588	10.971213
1	10011000	6.968432	10.909883	10.571676
6	10061003	6.286346	9.562762	9.005006
1	10011000	5.555971	10.253471	8.525923
1	10011000	7.266226	9.731738	8.505172
6	10061003	4.041454	6.674720	9.653860
1	10011000	2.961009	6.646525	9.917035

1	10011000	4.244715	5.846924	8.940543
6	10061003	4.388061	8.012284	8.999529
1	10011000	3.957442	8.811996	9.642028
1	10011000	3.889959	8.095701	8.007064
6	10061003	7.764034	6.963340	7.877814
1	10011000	8.078293	6.338208	7.013074
1	10011000	8.495550	7.792714	7.990499
6	10061003	6.368765	7.533849	7.635804
1	10011000	5.721336	6.689934	7.308646
1	10011000	6.391741	8.265537	6.796625
6	10061003	13.860427	0.675196	11.247056
1	10011000	14.499951	1.171736	10.484068
1	10011000	14.473382	0.519740	12.161048
6	10061003	13.367016	-0.672120	10.722743
1	10011000	12.973222	-0.499785	9.696578
6	10061003	11.761221	8.598382	9.310077
1	10011000	11.608174	9.547812	9.867192
1	10011000	11.264027	8.694782	8.319520
6	10061003	13.256282	8.342818	9.126399
1	10011000	13.749985	9.241330	8.691645
1	10011000	13.359670	7.526232	8.377792
6	10061003	14.453271	5.582437	10.185936
1	10011000	13.929797	5.417707	9.219428
1	10011000	15.295017	4.857824	10.249113
6	10061003	14.986257	7.013627	10.245081
1	10011000	15.572836	7.244160	9.327048
1	10011000	15.695552	7.063502	11.100752
6	10061003	14.136556	8.867545	12.694974
1	10011000	14.936708	8.166585	13.017007
1	10011000	14.247891	9.808757	13.277658
6	10061003	14.272699	9.154097	11.202177
1	10011000	15.316273	9.459636	10.962053
1	10011000	13.621112	10.027253	10.975813
6	10061003	12.595724	0.021574	19.815952
1	10011000	13.523945	-0.193083	19.241307
6	10061003	10.844408	3.030521	21.101005
1	10011000	10.080940	3.134452	21.903342
1	10011000	11.538531	3.896080	21.169806
6	10061003	11.621783	1.728985	21.280280
1	10011000	10.874332	0.919255	21.435026
1	10011000	12.242596	1.774927	22.203617
6	10061003	14.241757	2.546007	18.776978
1	10011000	15.125479	3.217519	18.852416
1	10011000	14.544904	1.639810	18.209411
6	10061003	13.766407	2.145662	20.171909
1	10011000	14.523881	1.495440	20.665317
1	10011000	13.700385	3.078351	20.775235
6	10061003	12.358319	10.179674	17.055781
1	10011000	11.629421	10.961896	16.752376
1	10011000	13.338664	10.424058	16.589995
6	10061003	12.489834	10.160015	18.577188
1	10011000	13.388039	9.549958	18.820139

1	10011000	12.684521	11.187354	18.960219
6	10061003	11.974122	7.421163	20.129849
1	10011000	12.985932	7.405310	19.670233
1	10011000	12.011481	6.822822	21.067059
6	10061003	11.570487	8.860796	20.439959
1	10011000	10.677804	8.815377	21.102561
1	10011000	12.374580	9.370253	21.017852
6	10061003	8.833978	9.961917	19.220444
1	10011000	8.050832	10.750419	19.171289
1	10011000	8.620219	9.319181	20.101610
6	10061003	10.213999	10.601776	19.373498
1	10011000	10.288135	11.406719	18.609160
1	10011000	10.301418	11.094520	20.368291
6	10061003	2.256713	3.968838	17.048746
1	10011000	1.781358	3.629410	16.103218
1	10011000	1.734749	4.892069	17.384473
6	10061003	2.128454	2.878060	18.110385
1	10011000	1.070219	2.540528	18.189725
1	10011000	2.393029	3.339417	19.087625
6	10061003	4.775723	1.802185	19.525387
1	10011000	4.486012	2.780003	19.967137
1	10011000	5.266231	1.197106	20.319635
6	10061003	3.531925	1.081433	19.009122
1	10011000	3.826138	0.028900	18.800630
1	10011000	2.750537	1.046172	19.801756
6	10061003	2.398424	0.790294	16.855900
1	10011000	1.665897	1.297669	16.189737
6	10061003	3.460238	0.158013	15.957631
1	10011000	4.076651	-0.552524	16.549591
1	10011000	2.974584	-0.410783	15.134154
1	10011000	1.839210	-0.000139	17.405971
1	10011000	12.662511	-0.561009	20.762614
6	10061003	11.420549	-0.473062	18.972920
1	10011000	11.617325	-1.506708	18.611755
1	10011000	10.498159	-0.493373	19.592636
1	10011000	9.098743	-0.692451	11.979236
1	10011000	14.218898	-1.382661	10.625363
7	10071003	11.671905	-0.417255	14.172684
1	10011000	10.818025	-0.331148	14.770167
1	10011000	12.473960	0.079705	14.624006
7	10071003	12.315596	-1.206498	11.618386
6	10061003	12.895070	-1.966048	12.750000
1	10011000	13.027347	-3.041589	12.493554
1	10011000	13.899661	-1.575240	13.025471
6	10061003	11.319347	-2.010052	10.873542
1	10011000	11.797367	-2.594959	10.055347
1	10011000	10.813476	-2.743442	11.539916
6	10061003	10.234949	-1.096091	10.305439
1	10011000	9.387769	-1.703812	9.917504
1	10011000	10.648606	-0.503979	9.460751
6	10061003	12.003524	-1.822680	13.982073
1	10011000	12.525694	-2.219588	14.880686

1	10011000	11.070040	-2.408763	13.839621

H. ONIOM optimized structure for the $[Mo(CuNL)_6(CN)_2]^{9+}$ (Mo^V)

42	10421006	8.647581	4.527896	14.529282
29	10291003	6.573240	5.545958	9.760681
29	10291003	11.417408	1.765464	10.891152
29	10291003	12.178352	7.999704	12.507458
29	10291003	11.825139	1.264246	17.311466
29	10291003	10.383961	7.681132	18.465774
29	10291003	5.136594	3.463219	18.359279
7	10071001	7.256530	5.148856	11.554210
7	10071001	10.421824	2.764290	12.257294
7	10071001	10.895886	6.712644	13.247350
7	10071001	10.628092	2.469544	16.334573
7	10071001	9.728497	6.455823	17.082010
7	10071001	6.452770	3.866670	16.963371
7	10071002	6.696186	7.165899	14.675725
7	10071002	6.950234	1.793417	13.879559
7	10071003	5.948743	5.938520	7.932222
7	10071003	5.039858	6.556915	10.463319
1	10011000	4.606639	6.063410	11.277052
1	10011000	5.352901	7.512393	10.751439
7	10071003	6.369203	3.628702	9.364223
1	10011000	7.169447	3.077522	9.749453
1	10011000	5.471231	3.281113	9.772715
7	10071003	8.250844	6.483571	9.322763
1	10011000	8.557819	7.091345	10.116527
1	10011000	8.996125	5.782731	9.105837
7	10071003	10.318611	2.560381	9.463134
1	10011000	9.410309	2.046512	9.396657
1	10011000	10.140500	3.574363	9.645694
7	10071003	10.906017	0.031979	11.668864
1	10011000	9.902058	0.032059	11.961124
7	10071003	13.472134	9.287941	11.762012
7	10071003	10.977687	9.508418	12.903545
1	10011000	10.235910	9.566914	12.168381
1	10011000	10.536450	9.399830	13.845178
7	10071003	12.110443	7.124475	10.744618
1	10011000	12.710668	6.267944	10.756099
1	10011000	11.129932	6.865548	10.490700
7	10071003	13.545233	7.463243	13.819170
1	10011000	13.351014	7.927304	14.736198
1	10011000	13.559141	6.424954	13.943138
7	10071003	13.049823	0.059294	18.277200
7	10071003	12.484265	0.496158	15.622015
1	10011000	11.694031	0.322605	14.959847
1	10011000	13.174745	1.149418	15.185348
7	10071003	10.318058	0.415827	18.250456
1	10011000	9.625232	1.131269	18.569175
1	10011000	9.851913	-0.271215	17.614252
7	10071003	12.756954	2.789944	18.137483
1	10011000	12.911942	3.555125	17.441928

1	10011000	12.192579	3.149891	18.941190
7	10071003	11.057130	8.919854	19.843805
7	10071003	10.807186	9.044171	17.108266
1	10011000	11.705024	8.796533	16.632163
1	10011000	10.040429	9.117200	16.400975
7	10071003	11.762209	6.390258	19.023754
1	10011000	11.330160	5.658000	19.632979
1	10011000	12.210993	5.941084	18.193096
7	10071003	8.634459	7.701609	19.367311
1	10011000	7.983414	8.339383	18.854171
1	10011000	8.227812	6.739835	19.412312
7	10071003	3.814251	3.058100	19.765943
7	10071003	5.482121	5.183605	19.252362
1	10011000	6.356647	5.108975	19.820961
1	10011000	5.575471	5.958500	18.556358
7	10071003	6.135874	1.857385	18.906896
1	10011000	5.929185	1.074194	18.245127
1	10011000	7.164512	2.044362	18.924844
7	10071003	3.692572	3.315232	17.029350
1	10011000	3.368408	4.271923	16.757788
1	10011000	4.016077	2.796233	16.181054
6	10061001	7.706823	4.929597	12.607079
6	10061001	9.824983	3.374251	13.052277
6	10061001	10.138402	5.943056	13.690894
6	10061001	9.936050	3.189271	15.730296
6	10061001	9.349398	5.755062	16.230443
6	10061001	7.224495	4.089540	16.118714
6	10061002	7.402796	6.206527	14.604303
6	10061002	7.559081	2.788390	14.133257
6	10061003	4.079300	6.656026	9.371514
1	10011000	3.497808	5.711428	9.302119
1	10011000	3.364975	7.487166	9.562440
6	10061003	4.826520	6.896978	8.058893
1	10011000	4.125324	6.818806	7.197322
1	10011000	5.193858	7.946946	8.079664
6	10061003	6.335042	3.507744	7.913324
1	10011000	5.891009	2.531406	7.619107
1	10011000	7.371242	3.550419	7.512937
6	10061003	5.510172	4.656209	7.335248
1	10011000	4.443361	4.445360	7.570983
1	10011000	5.597083	4.672047	6.225077
6	10061003	7.985583	7.302229	8.148372
1	10011000	8.940088	7.573070	7.644938
1	10011000	7.479901	8.242503	8.457072
6	10061003	7.088309	6.524105	7.189966
1	10011000	7.716086	5.731606	6.725012
1	10011000	6.740177	7.185934	6.364721
6	10061003	11.067085	2.404237	8.224025
1	10011000	10.388310	2.509780	7.349193
1	10011000	11.842991	3.197198	8.155970
6	10061003	11.732009	1.029562	8.211706
1	10011000	10.928823	0.278133	8.043134

6	10061003	11.799676	10.710710	12.877011
1	10011000	12.342672	10.810633	13.841762
1	10011000	11.159906	11.611341	12.746704
6	10061003	12.802480	10.608449	11.728699
1	10011000	13.539830	11.440885	11.786191
1	10011000	12.233296	10.747938	10.782927
6	10061003	12.634369	8.084753	9.782962
1	10011000	11.840217	8.815640	9.517469
1	10011000	12.948923	7.563805	8.851640
6	10061003	13.823434	8.817426	10.402287
1	10011000	14.139335	9.661198	9.747973
1	10011000	14.671808	8.098150	10.431563
6	10061003	14.826223	7.916749	13.294704
1	10011000	15.190985	7.196539	12.530814
1	10011000	15.580563	7.965457	14.110877
6	10061003	14.649671	9.294850	12.660205
1	10011000	15.575470	9.589934	12.116347
1	10011000	14.518963	10.023278	13.491031
6	10061003	13.907643	-0.597440	17.264435
1	10011000	14.806196	0.018190	17.037281
6	10061003	10.882991	-0.276066	19.401726
1	10011000	10.175924	-1.052418	19.768571
1	10011000	11.052718	0.450688	20.225300
6	10061003	12.209943	-0.921295	19.002674
1	10011000	11.968166	-1.797451	18.361136
1	10011000	12.732110	-1.316717	19.903343
6	10061003	14.038259	2.289362	18.616226
1	10011000	14.456298	2.976248	19.385309
1	10011000	14.757445	2.240420	17.770293
6	10061003	13.843331	0.894592	19.207783
1	10011000	14.830438	0.430176	19.431543
1	10011000	13.319897	1.022292	20.181193
6	10061003	10.951873	10.310202	17.813812
1	10011000	9.947650	10.745650	18.006359
1	10011000	11.526668	11.032571	17.193024
6	10061003	11.671374	10.068489	19.139127
1	10011000	12.739569	9.869955	18.899863
1	10011000	11.647519	10.989646	19.764344
6	10061003	12.758045	7.140395	19.777161
1	10011000	13.449780	7.651561	19.073180
1	10011000	13.359553	6.451946	20.410847
6	10061003	12.053057	8.177283	20.650075
1	10011000	11.566330	7.626666	21.485360
1	10011000	12.799057	8.864462	21.109416
6	10061003	8.864973	8.206800	20.714266
1	10011000	7.912574	8.577976	21.154214
1	10011000	9.244736	7.385278	21.359232
6	10061003	9.893241	9.336281	20.659705
1	10011000	9.384948	10.220017	20.214508
1	10011000	10.200778	9.626819	21.689663
6	10061003	4.344719	5.435186	20.126608
1	10011000	3.500862	5.844110	19.530047

1	10011000	4.614539	6.185538	20.902387
6	10061003	3.921055	4.124903	20.787702
1	10011000	2.961261	4.262679	21.335252
1	10011000	4.693260	3.877733	21.549651
6	10061003	5.671503	1.513364	20.244051
1	10011000	6.182155	2.157790	20.991848
1	10011000	5.918196	0.453671	20.476216
6	10061003	4.161449	1.730465	20.322886
1	10011000	3.682269	0.911639	19.741712
1	10011000	3.811674	1.625594	21.374903
6	10061003	2.480489	3.049457	19.122439
1	10011000	2.035478	4.069045	19.103106
6	10061003	2.607200	2.586597	17.672281
1	10011000	2.823536	1.496773	17.644503
1	10011000	1.651883	2.762138	17.130182
1	10011000	1.766159	2.397061	19.673967
1	10011000	14.275801	-1.585670	17.621945
6	10061003	13.134119	-0.763479	15.957675
1	10011000	13.824031	-1.069752	15.140552
1	10011000	12.366240	-1.558390	16.074868
1	10011000	11.517052	-0.175851	12.491566
1	10011000	12.433795	0.948821	7.350919
7	10071003	13.102861	2.624516	11.438092
1	10011000	13.180992	2.666357	12.480170
1	10011000	13.147134	3.590876	11.040118
7	10071003	12.424430	0.795753	9.499846
6	10061003	13.798917	1.346679	9.489202
1	10011000	14.534957	0.598376	9.117115
1	10011000	13.872774	2.231687	8.818909
6	10061003	12.411293	-0.636878	9.876063
1	10011000	12.513156	-1.293896	8.982854
1	10011000	13.257956	-0.883430	10.554461
6	10061003	11.121875	-0.965137	10.628683
1	10011000	11.189323	-1.980922	11.077616
1	10011000	10.263896	-0.956288	9.922287
6	10061003	14.182101	1.813031	10.892092
1	10011000	15.125141	2.402067	10.854579
1	10011000	14.352058	0.931525	11.547331

I. ONIOM final structure for the $[Mo(CuCNL)_6(CN)_2]^{8+}$ ($Mo^{IV,T}$) optimization, including in the QM region, in addition to the Mo and the eight CN fragments, one of the $[Cu(tris(2\text{-aminoethyl})amine)]^{+}$ ligands, in order to describe accurately the hydrogen bond formation. The initial structure for the optimization is the eight-coordinated complex and the final point is a seven-coordinated complex (structure shown here). The optimization stops because of the changes in the connectivity, which poses problems to the ONIOM calculation. Further optimization of this structure leads, as expected, to a similar seven-coordinated complex.

42	10421006	8.687726	4.551355	14.474994
29	10291003	7.567248	8.784308	12.391084
29	10291003	14.014347	0.667441	12.098417
29	10291003	12.713967	6.677931	11.818104
29	10291003	12.663898	3.022701	17.201079
29	10291003	10.647437	8.211273	17.873165

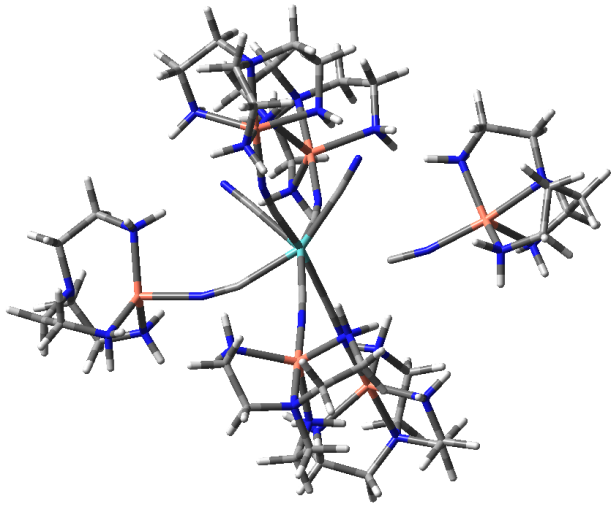
29	10291003	6.887647	2.723765	18.587134
7	10071001	7.625150	6.870968	12.640002
7	10071001	12.454470	1.690699	12.598056
7	10071001	11.117757	5.946189	12.619122
7	10071001	10.883417	3.246666	16.491106
7	10071001	10.046239	6.849712	16.622282
7	10071001	6.844021	3.356106	16.765163
7	10071001	7.019505	6.881646	16.286776
7	10071001	7.925018	2.060597	12.830724
7	10071003	7.542611	10.737365	12.113875
7	10071003	9.151603	9.026606	13.539844
1	10011000	9.078647	8.440936	14.401473
1	10011000	10.016160	8.769596	13.012009
7	10071003	5.771991	8.916553	13.185330
1	10011000	5.155277	8.140908	12.851582
1	10011000	5.848930	8.886087	14.228035
7	10071003	7.761711	8.570217	10.441666
1	10011000	8.456321	7.824179	10.209574
1	10011000	6.833252	8.327464	10.025652
7	10071003	13.684842	0.954788	10.180182
1	10011000	12.937428	0.301525	9.850655
1	10011000	13.402287	1.943481	9.990826
7	10071003	13.280498	-0.923818	13.000752
1	10011000	12.255840	-1.021896	12.816621
7	10071003	14.377887	7.407541	11.045899
7	10071003	11.697768	7.643126	10.439310
1	10011000	11.434493	6.985452	9.669882
1	10011000	10.839601	8.079247	10.843920
7	10071003	13.393679	4.872477	11.431391
1	10011000	13.777846	4.455637	12.309673
1	10011000	12.635860	4.263682	11.047111
7	10071003	13.171160	7.590012	13.501371
1	10011000	12.637237	8.487136	13.556653
1	10011000	12.954404	6.992606	14.331021
7	10071003	14.499905	2.909563	17.906388
7	10071003	12.914720	1.272735	16.341244
1	10011000	12.078426	0.662769	16.489534
1	10011000	13.075610	1.404939	15.318676
7	10071003	12.007737	3.053747	19.058644
1	10011000	11.235010	3.743690	19.185843
1	10011000	11.669110	2.099241	19.318870
7	10071003	13.206425	4.672321	16.259627
1	10011000	12.850184	4.667248	15.276275
1	10011000	12.827167	5.506307	16.762462
7	10071003	11.238423	9.578626	19.181323
7	10071003	12.019616	8.904314	16.618263
1	10011000	12.849580	8.270199	16.625810
1	10011000	11.640411	8.975496	15.650788
7	10071003	11.128737	6.824974	19.209826
1	10011000	10.268815	6.496319	19.698630
1	10011000	11.603603	6.017398	18.752916
7	10071003	8.843487	9.015648	17.898350

1	10011000	8.721682	9.610479	17.048749
1	10011000	8.105823	8.276402	17.922329
7	10071003	6.999509	2.093840	20.452808
7	10071003	4.928456	2.762620	18.755572
1	10011000	4.610842	3.746546	18.913707
1	10011000	4.470625	2.373635	17.899734
7	10071003	7.939321	4.303675	19.122818
1	10011000	8.930821	4.181967	18.817473
1	10011000	7.548180	5.176009	18.699471
7	10071003	7.776559	1.054157	18.032456
1	10011000	7.059816	0.382758	17.672563
1	10011000	8.494831	1.229887	17.294111
6	10061001	7.699981	5.726229	12.801685
6	10061001	11.516004	2.294420	12.903578
6	10061001	10.165459	5.505409	13.105846
6	10061001	9.824720	3.413258	16.055028
6	10061001	9.616269	6.045196	15.877030
6	10061001	6.857268	3.757427	15.678992
6	10061001	7.595933	6.061993	15.674501
6	10061001	7.487803	2.922041	13.467926
6	10061003	9.198727	10.434508	13.909584
1	10011000	8.504771	10.620746	14.756892
1	10011000	10.224620	10.712466	14.238334
6	10061003	8.783709	11.282290	12.710182
1	10011000	8.655532	12.345333	13.015946
1	10011000	9.625884	11.254533	11.983523
6	10061003	5.227090	10.201167	12.765116
1	10011000	4.393496	10.503407	13.436873
1	10011000	4.822931	10.113482	11.733537
6	10061003	6.334067	11.255014	12.795986
1	10011000	6.540184	11.482097	13.865291
1	10011000	5.977294	12.201390	12.329992
6	10061003	8.216692	9.851700	9.919932
1	10011000	8.016308	9.915547	8.827596
1	10011000	9.312668	9.949857	10.074458
6	10061003	7.490127	10.975959	10.653511
1	10011000	6.440852	10.984528	10.283551
1	10011000	7.934380	11.961160	10.384878
6	10061003	14.939101	0.658878	9.500727
1	10011000	14.755940	0.471671	8.419639
1	10011000	15.623490	1.530196	9.589204
6	10061003	15.583185	-0.568450	10.144832
1	10011000	14.982976	-1.453037	9.836101
6	10061003	12.585808	8.678789	9.928379
1	10011000	12.591818	9.541055	10.629890
1	10011000	12.225658	9.040456	8.940013
6	10061003	13.999852	8.111472	9.798274
1	10011000	14.720017	8.925178	9.554861
1	10011000	13.995163	7.417168	8.928983
6	10061003	14.451807	5.023285	10.442158
1	10011000	14.002598	5.134565	9.431772
1	10011000	15.101580	4.120965	10.430403

6	10061003	15.277497	6.262088	10.778137
1	10011000	15.988942	6.487072	9.951592
1	10011000	15.890471	6.013113	11.672957
6	10061003	14.597924	7.870579	13.450434
1	10011000	15.166636	6.948907	13.700071
1	10011000	14.862476	8.654252	14.194454
6	10061003	14.959904	8.335434	12.042694
1	10011000	16.065567	8.411526	11.934113
1	10011000	14.553080	9.364225	11.922234
6	10061003	15.136240	1.745613	17.247844
1	10011000	15.591806	2.033542	16.276161
6	10061003	13.142367	3.416678	19.896582
1	10011000	12.952080	3.119449	20.951519
1	10011000	13.288297	4.517642	19.871096
6	10061003	14.395593	2.719249	19.371590
1	10011000	14.305515	1.641996	19.634055
1	10011000	15.298499	3.103260	19.898330
6	10061003	14.661696	4.723769	16.251380
1	10011000	15.008236	5.771298	16.107679
1	10011000	15.054431	4.119359	15.407147
6	10061003	15.190669	4.175275	17.572027
1	10011000	16.293677	4.033375	17.515578
1	10011000	15.002974	4.952209	18.346216
6	10061003	12.403990	10.239892	17.104563
1	10011000	11.655970	10.985957	16.767006
1	10011000	13.391348	10.535241	16.687703
6	10061003	12.466842	10.220122	18.634939
1	10011000	13.376037	9.656497	18.928084
1	10011000	12.590194	11.255036	19.026829
6	10061003	12.036805	7.461721	20.176151
1	10011000	13.062681	7.499651	19.756981
1	10011000	12.074602	6.872833	21.118296
6	10061003	11.536021	8.876925	20.461414
1	10011000	10.624205	8.786222	21.088355
1	10011000	12.285234	9.436794	21.063672
6	10061003	8.770821	9.835547	19.104886
1	10011000	7.947409	10.578705	19.011058
1	10011000	8.549383	9.189505	19.978490
6	10061003	10.111856	10.553045	19.312934
1	10011000	10.182508	11.353809	18.547905
1	10011000	10.124420	11.055260	20.304894
6	10061003	4.598223	1.941490	19.913874
1	10011000	4.601973	0.869129	19.621911
1	10011000	3.580295	2.192823	20.285505
6	10061003	5.632135	2.178136	21.015943
1	10011000	5.486849	1.446708	21.842966
1	10011000	5.432628	3.186479	21.441052
6	10061003	7.873593	4.390610	20.575191
1	10011000	6.921891	4.879098	20.876201
1	10011000	8.713441	5.007531	20.963567
6	10061003	7.942320	2.985359	21.165510
1	10011000	8.992392	2.634605	21.052232

1	10011000	7.727175	3.015266	22.257644
6	10061003	7.491447	0.697583	20.419122
1	10011000	6.652093	-0.023870	20.305703
6	10061003	8.415739	0.504777	19.219841
1	10011000	9.378103	1.029630	19.399842
1	10011000	8.634172	-0.576257	19.074485
1	10011000	8.021599	0.428711	21.360838
1	10011000	15.956853	1.325224	17.872138
6	10061003	14.089687	0.666400	16.957494
1	10011000	14.520216	-0.107822	16.284647
1	10011000	13.795465	0.167654	17.906034
1	10011000	13.448773	-0.852075	14.030327
1	10011000	16.610214	-0.720355	9.742125
7	10071003	15.219594	1.894271	13.056240
1	10011000	14.797698	2.219920	13.952987
1	10011000	15.439368	2.716694	12.450414
7	10071003	15.595185	-0.416137	11.618119
6	10061003	16.791461	0.324047	12.082431
1	10011000	17.638264	-0.364161	12.304680
1	10011000	17.151755	1.036509	11.307204
6	10061003	15.464932	-1.721818	12.304306
1	10011000	15.998045	-2.528499	11.751921
1	10011000	15.904417	-1.686455	13.326210
6	10061003	13.989816	-2.075880	12.463110
1	10011000	13.876671	-2.949379	13.142640
1	10011000	13.561038	-2.348527	11.474625
6	10061003	16.439222	1.145769	13.320204
1	10011000	17.271119	1.840715	13.570058
1	10011000	16.279238	0.469628	14.187625

J. DFT optimized $[Mo(CN)_2(CN\text{-}Cu(tris(2\text{-}aminoethyl)amine)_6]^{8+}$ for S = 4, with a seven coordinated Mo.



Mo	9.281782	4.484088	14.436141
Cu	6.103609	6.769926	10.854114
Cu	10.103122	0.281830	11.216627
Cu	13.519187	7.239424	12.181633

Cu	13.048179	2.388960	17.950508
Cu	9.149407	9.291081	17.846777
Cu	5.698802	2.054758	17.511131
N	7.710293	6.312728	12.074369
N	10.365653	1.852755	12.515508
N	11.981770	6.164899	13.038495
N	11.700232	3.255410	16.653907
N	9.841546	7.720053	16.741044
N	7.439302	2.527767	16.496351
N	6.776098	6.056801	16.033804
N	6.964153	2.930709	12.710740
N	4.295222	7.106649	9.633994
N	5.573791	8.736779	11.603494
H	5.737397	8.853629	12.613827
H	6.150138	9.463922	11.151531
N	4.981777	5.143129	11.567088
H	5.567986	4.312497	11.784402
H	4.561194	5.419042	12.466862
N	7.049079	6.881021	8.944236
H	7.915294	7.436565	8.927205
H	7.338401	5.928578	8.675086
N	11.094242	1.080634	9.496379
H	10.541157	1.883402	9.161713
H	12.030394	1.461372	9.692623
N	8.026678	0.237670	11.530261
H	7.623107	1.172798	11.750430
N	15.138416	8.415060	11.227876
N	12.337464	8.312773	10.781031
H	12.103714	7.681385	10.000259
H	11.434269	8.605770	11.180110
N	14.737449	5.615553	11.512586
H	15.291887	5.253377	12.303783
H	14.186997	4.811499	11.180440
N	14.212458	8.291846	13.916806
H	13.545775	9.054062	14.113506
H	14.216563	7.720267	14.773495
N	14.507189	1.445963	19.372584
N	12.452328	0.346363	17.723748
H	11.431129	0.244436	17.636666
H	12.842986	-0.012099	16.838816
N	12.464971	3.417856	19.729797
H	12.243478	4.408601	19.558782
H	11.592061	3.003282	20.088800
N	14.855421	2.981961	16.988762
H	14.791437	2.930528	15.962808
H	15.010534	3.977076	17.211364
N	8.178348	10.789709	19.159007
N	9.933875	11.166621	16.924583
H	10.899528	11.346351	17.241546
H	9.994565	11.159052	15.896757
N	10.255732	8.914340	19.594248
H	9.952430	7.972086	19.883161

H	11.272998	8.841684	19.449109
N	7.175833	8.956095	17.258009
H	6.968985	9.517958	16.419781
H	7.025763	7.959294	16.985199
N	3.712906	1.751084	18.393219
N	5.320863	4.061052	17.966084
H	5.758596	4.295877	18.869124
H	5.732844	4.729134	17.280018
N	6.301968	0.874310	19.275262
H	6.479233	-0.108513	19.013849
H	7.168342	1.185581	19.735039
N	4.905484	0.787156	16.015346
H	4.804753	1.378641	15.175302
H	5.545319	0.030190	15.734490
C	8.349747	5.739573	12.889068
C	10.195976	2.789946	13.221485
C	11.045509	5.607172	13.502394
C	10.881466	3.700001	15.923191
C	9.997299	6.739146	16.088304
C	8.169576	3.132948	15.788726
C	7.683209	5.566506	15.450553
C	7.776092	3.484322	13.371361
C	4.137699	8.979769	11.276964
H	3.514969	8.414165	11.999064
H	3.848113	10.046885	11.387881
C	3.874256	8.528338	9.845513
H	2.799581	8.648656	9.581542
H	4.438253	9.169255	9.140003
C	3.916244	4.832147	10.578093
H	3.141839	4.147494	10.986077
H	4.384371	4.305609	9.721642
C	3.268221	6.134478	10.129616
H	2.734288	6.602972	10.980986
H	2.503114	5.955936	9.341272
C	6.083473	7.408880	7.934967
H	6.382930	7.168818	6.892959
H	6.079802	8.515020	8.003832
C	4.704275	6.836490	8.223479
H	4.705928	5.737748	8.071604
H	3.945799	7.246566	7.518460
C	11.174493	0.040778	8.427786
H	11.333668	0.476828	7.418663
H	12.060209	-0.593202	8.629325
C	9.893251	-0.782315	8.437460
H	9.031353	-0.148763	8.145641
C	13.103999	9.484838	10.266749
H	13.061736	10.290024	11.028717
H	12.665158	9.907435	9.337596
C	14.541329	9.050240	10.011115
H	15.166750	9.910584	9.680299
H	14.575920	8.313814	9.181604
C	15.659232	6.107084	10.447386

H	15.079462	6.205812	9.507526
H	16.488466	5.399894	10.234606
C	16.230000	7.452128	10.881861
H	16.881827	7.880397	10.087287
H	16.874231	7.320705	11.774609
C	15.563912	8.859363	13.645093
H	16.308468	8.045876	13.763671
H	15.849114	9.650286	14.370803
C	15.578029	9.431340	12.233861
H	16.589784	9.814775	11.970268
H	14.889586	10.298080	12.173970
C	14.405538	-0.030038	19.159612
H	15.060276	-0.312334	18.308474
C	13.545405	3.287910	20.750461
H	13.198990	3.542413	21.775666
H	14.343529	4.019494	20.509818
C	14.075807	1.858528	20.741131
H	13.294310	1.154901	21.093591
H	14.924726	1.757289	21.455888
C	15.987981	2.154993	17.495659
H	16.980825	2.593808	17.259521
H	15.955476	1.174360	16.978045
C	15.846086	1.999446	19.004107
H	16.647649	1.342597	19.412258
H	15.972312	2.984380	19.499873
C	9.066747	12.292061	17.371355
H	8.135527	12.277946	16.769172
H	9.527275	13.289038	17.199447
C	8.768823	12.129551	18.856771
H	9.708912	12.234247	19.431235
H	8.093831	12.938776	19.216695
C	9.951378	9.911027	20.660585
H	10.632358	10.775469	20.530437
H	10.153350	9.518667	21.679598
C	8.491113	10.334700	20.545999
H	7.824796	9.480054	20.783797
H	8.258530	11.134438	21.285430
C	6.289971	9.361970	18.378202
H	5.214901	9.377651	18.095904
H	6.397529	8.607224	19.185543
C	6.713684	10.746790	18.855795
H	6.508783	11.486897	18.055763
H	6.123413	11.071422	19.741700
C	3.841581	4.220593	18.055970
H	3.434479	4.193887	17.023852
H	3.537489	5.200197	18.482548
C	3.271407	3.091539	18.902373
H	2.159885	3.135038	18.940709
H	3.619601	3.190323	19.950175
C	5.170057	0.919970	20.244576
H	5.207767	1.896100	20.771957
H	5.248385	0.144797	21.036532

C	3.853925	0.748514	19.493176
H	3.802215	-0.269131	19.055625
H	2.991311	0.827834	20.193049
C	2.854475	1.260630	17.273985
H	2.574961	2.129406	16.644778
C	3.587188	0.225769	16.431883
H	3.776872	-0.703467	17.005616
H	2.957487	-0.066192	15.564879
H	1.902110	0.842449	17.672670
H	14.812218	-0.564808	20.048841
C	12.970261	-0.453635	18.870687
H	12.931042	-1.548707	18.688769
H	12.307196	-0.271493	19.742788
H	7.858913	-0.323995	12.379886
H	9.950069	-1.605114	7.688618
N	11.299912	-1.293784	12.109575
H	11.318009	-1.276216	13.138517
H	12.285409	-1.196273	11.817846
N	9.622039	-1.340990	9.797452
C	10.513534	-2.499606	10.124523
H	10.074578	-3.444463	9.732885
H	11.474647	-2.367043	9.588554
C	8.174319	-1.663829	10.004552
H	7.763184	-2.161443	9.097977
H	8.097015	-2.407176	10.825416
C	7.381978	-0.412618	10.361011
H	6.319896	-0.677274	10.552723
H	7.379939	0.310467	9.519424
C	10.765972	-2.597674	11.623521
H	11.454101	-3.445923	11.830048
H	9.826690	-2.812897	12.173587

K. One of the Cu^{TB}-Mo^{D} dimers (dimer 5 according to Figure S1) obtained by overlaying the optimized fragments and fixing the Cu-N-C, Mo-C-N angles, as well as the torsion angle, according to the ONIOM optimized structure (F):

Mo	-1.96873	1.88535	0.12516
Cu	1.83368	-1.80163	-0.13116
N	-1.90900	2.11490	3.43811
N	-3.66972	-0.74144	1.31613
N	-5.06034	3.06422	-0.17566
N	-2.85429	0.36695	-2.72508
N	-0.74518	3.71520	-2.36272
N	1.05795	2.99088	1.03832
N	-2.28899	5.11537	0.95012
N	0.41887	-0.41211	-0.02965
N	3.33111	-3.24881	-0.2441
N	1.33968	-2.69833	1.7084
N	3.41051	-0.40786	-0.2124
N	1.12107	-2.64765	-1.9262
C	-1.95579	1.99289	2.26213
C	-2.16995	3.95654	0.65547
C	-3.06896	0.18531	0.89105

C	-3.95195	2.65516	-0.06354
C	-2.54339	0.90058	-1.71562
C	-1.19892	3.03339	-1.50875
C	-0.02953	2.59790	0.71150
C	-0.41887	0.41211	0.02965
C	3.04108	-4.26431	0.84841
C	2.50156	-3.57315	2.10359
C	4.63777	-1.14854	-0.67699
C	4.65209	-2.53139	-0.01968
C	1.78947	-3.98938	-2.08169
C	3.24684	-3.86282	-1.63079
H	-5.97274	3.51047	-0.23788
H	-3.11180	-0.07714	-3.60556
H	-4.18317	-1.53248	1.70264
H	-1.82342	2.29090	4.43727
H	-0.32417	4.35242	-3.03601
H	3.19458333	0.39100798	-0.83926447
H	3.55294390	-0.00343453	0.73535038
H	0.08710325	-2.74053403	-1.93253238
H	1.36167187	-2.01591189	-2.71673916
H	1.13036082	-1.99600159	2.44379695
H	0.47312273	-3.26081205	1.58741517
H	5.57712110	-0.60030720	-0.43343520
H	4.59336364	-1.22176636	-1.78596317
H	5.49035982	-3.15566665	-0.41105042
H	4.80788963	-2.43414523	1.07801558
H	1.74500991	-4.36231032	-3.13101967
H	1.23020513	-4.72398284	-1.46099738
H	3.75900869	-4.85451878	-1.63528892
H	3.80984294	-3.20529802	-2.33011766
H	3.27170134	-2.92547877	2.57840056
H	2.21482361	-4.33422118	2.86580284
H	3.96455524	-4.84920545	1.07476422
H	2.29182510	-4.98669643	0.45294525

L. One of the Cu^{TB}-Mo^{SA} dimers (dimer 5 according to Figure S1) obtained by overlaying the optimized fragments and fixing the Cu-N-C, Mo-C-N angles, as well as the torsion angle, according to the ONIOM optimized structure (G):

Mo	2.89845000	0.01482000	0.03596000
Cu	-2.45301000	0.13583000	0.25653000
N	2.61310000	1.37443000	3.06037000
N	2.00716000	-2.60774000	2.06911000
N	1.88063000	-0.42290000	-3.21694000
N	5.10712000	1.73843000	-1.76149000
N	4.65071000	-2.77988000	-1.09055000
N	5.81562000	-0.16998000	1.57326000
N	1.79118000	3.10275000	-0.34707000
N	-0.59132000	0.03209000	0.06091000
N	-5.24395682	0.30699172	0.54127050
N	-2.96906526	-1.06406541	1.92169625
N	-3.29729740	-0.61935205	-1.53162279
N	-2.91247792	2.17701763	0.55035075

C	2.73016000	0.85511000	2.00696000
C	2.19120000	1.98469000	-0.16315000
C	2.20348000	-1.68669000	1.35433000
C	2.29574000	-0.36416000	-2.11150000
C	4.29184000	1.13934000	-1.15367000
C	3.97807000	-1.91177000	-0.65239000
C	4.77417000	-0.08029000	0.98056000
C	0.59132000	-0.03209000	-0.06091000
C	-5.42378986	-0.54349960	1.72886935
C	-4.34926326	-1.64115711	1.87111782
C	-4.62944529	-0.03299435	-1.88185228
C	-5.66162140	-0.24930184	-0.75581238
C	-4.14697258	2.42602936	1.35953735
C	-5.38622481	1.76006982	0.72722639
H	5.26993000	-3.51830000	-1.43499000
H	1.51231000	-0.45288000	-4.17151000
H	1.85852000	-3.40463000	2.69412000
H	2.55799000	1.86749000	3.95480000
H	5.81947000	2.29780000	-2.23671000
H	-2.60477062	-0.42307174	-2.27764131
H	-3.36558432	-1.65235683	-1.45000977
H	-2.08277175	2.59094422	1.01407213
H	-2.99185181	2.62886477	-0.38141625
H	-2.25959793	-1.81916990	1.95278287
H	-2.84232602	-0.49767263	2.78277411
H	-5.04057858	-0.46130108	-2.82991803
H	-4.47835408	1.05617109	-2.06194347
H	-6.64503980	0.16963324	-1.10075789
H	-5.82996426	-1.34489834	-0.62715622
H	-4.35377314	3.51816014	1.48442820
H	-3.96628240	2.01557872	2.37947020
H	-6.28026132	2.02235847	1.35484653
H	-5.57381683	2.22227646	-0.27118065
H	-4.39054264	-2.33370403	0.99935616
H	-4.58206094	-2.25277445	2.77828597
H	-6.43146540	-1.03976121	1.74786381
H	-5.39268554	0.11008599	2.63283358

M. One of the Cu^{TD}-Mo^{D} dimers (dimer 5 according to Figure S1) obtained by overlaying the optimized fragments and fixing the Cu-N-C, Mo-C-N angles, as well as the torsion angle, according to the ONIOM optimized structure (H):

Mo	2.49128	0.44295	1.16688
Cu	-2.22882	-0.43969	-0.96980
N	0.39364	2.06056	3.22024
N	2.01172	3.09425	-0.86824
N	5.51380	0.99712	-0.22861
N	2.97308	-2.20275	-0.87494
N	4.58616	-1.18082	3.21813
N	0.93617	-1.89118	2.92642
N	4.04391	2.77202	2.93529
N	-0.55065683	-0.14984895	-0.18580358
N	-4.74453624	-0.87372119	-2.14563184

N	-2.62213067	1.23647304	-2.20050791
N	-3.62707304	-0.58148361	0.61304373
N	-2.08738774	-2.23981736	-2.06683011
C	1.12753	1.51610	2.47653
C	3.46006	1.92435	2.29912
C	2.16253	2.14408	-0.18688
C	4.45297	0.78282	0.23590
C	2.82167	-1.25444	-0.19114
C	3.85308	-0.63414	2.47528
C	1.52102	-1.04175	2.29353
C	0.51640898	0.03342896	0.30955173
C	-4.84674648	0.34335312	-2.96683582
C	-4.07459801	1.54643161	-2.38712918
C	-4.81651567	-1.43919134	0.31196397
C	-5.57773866	-0.94152950	-0.93424277
C	-2.99774987	-2.31829780	-3.25251903
C	-4.47547228	-2.13845168	-2.84870756
H	6.44244	1.20578	-0.61464
H	3.09797	-3.03771	-1.45978
H	1.88728	3.93080	-1.45089
H	-0.21270	2.53644	3.89787
H	5.19189	-1.65870	3.89489
H	-3.10146708	-0.95803507	1.42335543
H	-3.92775697	0.37857358	0.87050650
H	-1.09650135	-2.31523364	-2.36218093
H	-2.26779881	-3.03014748	-1.41762842
H	-2.13449869	2.03347991	-1.75162164
H	-2.16180226	1.08154599	-3.11833251
H	-5.53043267	-1.48391913	1.17197274
H	-4.44706228	-2.47761779	0.14850867
H	-6.47943851	-1.59631526	-1.07505590
H	-5.97701436	0.07992545	-0.72828154
H	-2.89290416	-3.28877313	-3.79866849
H	-2.69122313	-1.51636586	-3.96268503
H	-5.10477511	-2.25316443	-3.77218111
H	-4.77064638	-2.97977814	-2.17738725
H	-4.48825853	1.82359802	-1.39045267
H	-4.23299669	2.42819962	-3.05691868
H	-5.91265455	0.65979774	-3.12729257
H	-4.44477367	0.11288167	-3.98202885

N. Optimized Cu^{TB}-Mo^{SA} dimer 2 with seven-coordinated Mo. Similar result is obtained for dimers 4, 5 and 6.

42	0.612406	1.987664	-1.406392
29	-0.758021	-2.077826	1.648980
7	0.249830	3.797542	1.390572
7	-2.306387	1.955170	-3.020374
7	0.980350	3.641092	-6.206413
7	3.527491	3.428856	-2.156693
7	1.567445	-0.151985	-3.798049
7	2.668273	0.192366	0.482043
7	-0.084984	5.059526	-2.352788

7	-0.799609	-0.503610	0.340145
7	-0.600956	-3.753849	2.979404
7	-2.514398	-1.608081	2.818664
7	1.146132	-1.562548	2.432682
7	-1.136199	-3.580185	0.164260
6	-0.428779	0.403373	-0.343516
6	0.345333	3.129908	0.421084
6	0.179551	3.928890	-2.041637
6	-1.273003	1.963357	-2.449833
6	0.965192	2.960323	-5.231012
6	2.490926	2.926318	-1.907271
6	1.191972	0.627051	-2.993694
6	2.048536	0.917585	-0.236308
6	-1.877949	-3.786036	3.798612
6	-2.379822	-2.371604	4.107395
6	1.726269	-2.808415	3.041904
6	0.630136	-3.519035	3.838647
6	-1.375159	-4.887227	0.870699
6	-0.452155	-4.972894	2.089850
1	1.780401	-1.134217	1.711968
1	0.986874	-0.831301	3.154954
1	-1.934484	-3.305309	-0.438229
1	-0.286153	-3.610253	-0.432498
1	-2.585651	-0.585094	2.973820
1	-3.353728	-1.898607	2.278981
1	2.593882	-2.581967	3.705394
1	2.118058	-3.443963	2.216942
1	0.991762	-4.492857	4.248486
1	0.324814	-2.898073	4.710704
1	-1.198272	-5.762321	0.202560
1	-2.447412	-4.926959	1.162835
1	-0.659665	-5.897576	2.681785
1	0.611097	-5.029665	1.765747
1	-1.668723	-1.818217	4.760280
1	-3.344154	-2.430191	4.665205
1	-1.702956	-4.360824	4.739942
1	-2.647564	-4.345415	3.221833
1	1.906063	-0.740844	-4.562034
1	-3.180886	2.031411	-3.545871
1	0.992081	4.229779	-7.040619
1	0.172830	4.439711	2.183451
1	4.413268	3.891386	-2.378308

O. Optimized Cu^{TB}-Mo^{SA} dimer1 with eight-coordinated Mo. A similar result is obtained for dimer 3.

42	0.088534	-1.059029	-2.314964
29	-0.386513	0.617793	2.450605
7	-0.807772	-4.212219	-1.569115
7	-3.251751	-1.080541	-3.007725
7	-0.258416	-2.013588	-5.588199
7	1.451525	1.435676	-4.127086
7	2.857258	-2.886916	-2.992782
7	2.592912	0.107307	-0.452978

7	-1.274579	1.784983	-1.161735
7	-0.467484	-0.781613	0.976706
7	-0.229124	2.034262	4.070284
7	1.376315	1.548718	1.788545
7	-0.976981	-0.718244	3.966520
7	-1.938420	1.940772	1.717104
6	-0.864071	0.808587	-1.715906
6	-0.521300	-3.079706	-1.765411
6	-2.083408	-1.146471	-2.823745
6	-0.078618	-1.606759	-4.490348
6	0.953490	0.587617	-3.471726
6	1.831888	-2.336965	-2.771397
6	1.795585	-0.348204	-1.220243
6	-0.295156	-1.007563	-0.185540
6	1.045457	2.835524	3.853730
6	2.059803	2.032299	3.034024
6	-1.171983	0.028060	5.261218
6	-0.171424	1.186295	5.325969
6	-1.824397	3.204431	2.508051
6	-1.479107	2.886000	3.971342
1	3.769122	-3.322573	-3.151225
1	-4.255930	-0.978972	-3.170386
1	-0.410531	-2.355850	-6.540719
1	-1.050816	-5.191255	-1.403310
1	1.880086	2.188825	-4.669521
1	-1.823135	-1.244584	3.676193
1	-0.194040	-1.402261	4.019180
1	-1.782378	2.067846	0.681426
1	-2.844712	1.454684	1.860189
1	1.973368	0.910842	1.197722
1	1.094632	2.336534	1.170830
1	-1.037670	-0.638233	6.144915
1	-2.223980	0.385796	5.296651
1	-0.359671	1.825491	6.223299
1	0.868180	0.796940	5.418504
1	-2.770452	3.796557	2.475335
1	-1.046328	3.841647	2.032171
1	-1.336938	3.825852	4.558323
1	-2.316581	2.331967	4.449538
1	2.434114	1.143850	3.590475
1	2.951466	2.661182	2.798573
1	1.469565	3.140633	4.839412
1	0.777428	3.772385	3.316347

S3. Absolute CASSCF and CASPT2 energies

Table S3. Absolute energies in a.u. of the five lowest doublet states calculated by using the CAS(3,3) level and the basis set shown in Table S1, for one of the Cu_{TB}-Mo_D dimers (dimer 5 according to Figure S1).

State	SA-CASSCF	CASPT2
Cu^{II}-$Mo^{IV\text{-}CS}$	-6895.1928590	-6899.1838542
Cu^{II}-$Mo^{IV\text{-}T}$	-6895.1138200	-6899.0908643
Cu^{II}-$Mo^{IV\text{-}OS}$	-6895.0902880	-6899.0725897
Cu^{II}-$Mo^{IV\text{-}CS*}$	-6894.9416940	-6898.9188689
MMCT	-6894.7578030	(a)

a) CASPT2(3,3) calculation for the MMCT state was not successful because of intruder state problems.

Table S4. Absolute energies in a. u. of the five lowest doublet states calculated by using the CAS(3,3) level and the basis set shown in Table S1, for one of the Cu_{TB}-Mo_{SA} dimers (dimer 5 according Figure S1).

State	SA-CASSCF	CASPT2
Cu^{II}-$Mo^{IV\text{-}CS}$	-6895.1664640	-6899.1065095
Cu^{II}-$Mo^{IV\text{-}T}$	-6895.1629010	-6899.0891151
Cu^{II}-$Mo^{IV\text{-}OS}$	-6895.1323050	-6899.0644945
Cu^{II}-$Mo^{IV\text{-}CS*}$	-6895.0546050	-6898.9792330
MMCT	-6894.7594210	(a)

a) CASPT2(3,3) calculation for the MMCT state was not successful because of intruder state problems.

Table S5. Absolute energies in a. u. of the five lowest doublet states calculated by using the CAS(3,3) level and the basis set shown in Table S1, for one of the Cu_{TD}-Mo_{SA} dimers (dimer 5 according Figure S1).

State	SA-CASSCF	CASPT2
Cu^{II}-$Mo^{IV\text{-}CS}$	-6895.1864530	-6899.1397170
Cu^{II}-$Mo^{IV\text{-}T}$	-6895.1150140	-6899.0591778
Cu^{II}-$Mo^{IV\text{-}OS}$	-6895.0849870	-6899.0346484
Cu^{II}-$Mo^{IV\text{-}CS*}$	-6894.9369450	-6898.8832756
MMCT	-6894.7834510	(a)

a) CASPT2(3,3) calculation for the MMCT state was not successful because of intruder state problems.

Table S6. Absolute energies in a. u. of the five lowest doublet states calculated by using the CAS(3,3) level and the basis set shown in Table S1, for one of the Cu_{TB}-Mo_{SA} optimized dimers (dimer 2 according Figure S1) in which Mo is seven-coordinated.

State	SA-CASSCF	CASPT2
Cu^{II}-$Mo^{IV\text{-}T}$	-6895.227059	-6899.133391
Cu^{II}-$Mo^{IV\text{-}CS}$	-6895.194917	-6899.107779
Cu^{II}-$Mo^{IV\text{-}OS}$	-6895.191826	-6899.102881
Cu^{II}-$Mo^{IV\text{-}CS*}$	-6895.152854	-6899.068363
MMCT	-6894.817381	(a)

a) CASPT2(3,3) calculation for the MMCT state was not successful because of intruder state problems.

Table S7. Absolute energies in a. u. of the five lowest doublet states calculated by using the CAS(3,3) level and the basis set shown in Table S1, for one of the Cu_{TB}-Mo_{SA} optimized dimers (dimer 2 according Figure S1) in which Mo is eight-coordinated.

State	SA-CASSCF	CASPT2
Cu^{II}-$Mo^{IV\text{-}CS}$	-6895.188998	-6899.1422538

Cu^{II}-$Mo^{IV\text{-}T}$	-6895.173625	-6899.1194506
Cu^{II}-$Mo^{IV\text{-}OS}$	-6895.143300	-6899.0942095
Cu^{II}-$Mo^{IV\text{-}CS*}$	-6895.063635	-6899.0032938
MMCT	-6894.808241	(a)

a) CASPT2(3,3) calculation for the MMCT state was not successful because of intruder state problems.

Table S8. Absolute energies in a. u. of the lowest energy doublet and quartet states, calculated at CASSCF and CASPT2 level, using a CAS(3,11) and the basis set shown in Table S2, for the optimized dimer with Mo seven-coordinated.

State	SA-CASSCF	CASPT2
Doublet Cu^{II}-$Mo^{IV\text{-}T}$	-6895.285375	-6899.377433
Quartet Cu^{II}-$Mo^{IV\text{-}T}$	-6895.285407	-6899.377593

Table S9. Relative CASPT2 energy (in eV) of the fifth doublet state (the MMCT state) with respect the ground state calculated by using the CAS(3,3) level and the basis set shown in Table S1, for one of the Cu_{TB}-Mo_D dimers (dimer 5 according to Figure S1). Relative energies of the rest of the states do not change more than 0.1 eV. At CASSCF level ΔE is 11.8 eV

Imaginary shift	ΔE CASPT2	reference weight	CASPT2 convergence
0	4.4	0.01498	NO
0.1	2.7	0.17710	NO
0.2	-7.7	0.16753	NO
0.3	-4.7	0.27052	NO
0.4	3.9	0.40598	YES
0.5	4.5	0.42531	YES
0.6	5.0	0.44178	YES
0.7	5.3	0.45768	YES
0.8	5.7	0.47354	YES
0.9	6.0	0.48947	YES

Table S10. Absolute energies in a.u. and relative energies to the ground state in eV of the nine lowest doublet states calculated by using the CAS(11,12) level and the basis set shown in Table S1, for one of the Cu_{TB}-Mo_D dimers (dimer 5 according to Figure S1).

State	SA-CASSCF	CASPT2	ΔE SA-CASSCF	ΔE CASPT2
ground state	-6895.380424	-6899.120492	0.00	0.00
Cu-Cu	-6895.344255	-6899.070475	0.98	1.36
Cu-Cu	-6895.344024	-6899.070898	0.99	1.35
Cu-Cu	-6895.335862	-6898.938284	1.21	4.96
Mo-Mo	-6895.335510	-6899.058970	1.22	1.67
Mo-Mo	-6895.289745	-6899.021469	2.47	2.69
Mo-Mo, Cu-Cu	-6895.261506	-6899.002254	3.24	3.22
Mo-Mo, Cu-Cu	-6895.253704	-6898.971244	3.45	4.06
Mo-Mo, Cu-Cu	-6895.253477	-6898.971615	3.45	4.05

Figure S2. Active orbitals used in the calculations CAS(11,12) on the model dimers.