Electronic properties of PrP^C-Cu(II) complex as marker of 5-fold Cu(II) coordination

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1. FEFF calculated spectra and corresponding IDOS functions for Cu(II)-phtalocyanine



derivative without H₂O and with 2 axial H₂O molecules.

Fig. S1. A – FEFF calculated spectrum and corresponding DOS functions for Cu(II)-phthalocyanine x 2H₂O compound; B - A – FEFF calculated spectrum and corresponding IDOS functions for Cu(II)-phthalocyanine compound.

Spectra in Fig. S1 A and S1 B were calculated with the same FEFF parameters as spectrum for Cu(II)-phthalocyanine x H_2O in Fig. 4 B. All calculated spectra exhibit pre-edge structure, and pronounced unoccupied Cu dDOS in range of -18 to -5 eV. In DOS functions in Fig S1 B, there is not enough electron density in comparison to experimental spectrum, in range where 1s -> 4p + LMCT transition should occur. Moreover edge position is significantly shifted. On the contrary in Fig. S1 A, for double hydrated complex, there is strong multielectron transition which give a rise to peak with maximum around 5 eV.

Solvent coordination of planar Cu(I)/Cu(II) complexes was deeply discussed by Penfold et al. in ¹. However all solvents included in analysis were non-aqueous and had significantly different properties than water, eg. the molecular weight or dipole moment. In such case, Cu(II) complex was not planar and Cu(II) 1st coordination shell was composed of 4 equivalent N atoms. When Cu(II) formed planar complex in aqueous solution, additional H2O molecule was reported ². Solvent composed of small molecule like H₂O has different properties than solvent composed of larger molecules when considered parallel and antiparallel coordination schemes ³. It was shown that antiparallel coordination of planar complex is possible in case of Cu(I)/Cu(II) planar organic complexes ⁴.

2. General structure of ORCA input file:

! UKS BP86 RI SV(P) Opt TightSCF Grid4 NoFinalGrid

%geom GDIISMaxEq 20 UseGDIIS true MaxIter 1000 end %scf MaxCore 4096 MaxIter 1000 end * xyzfile *x y* filename.xyz # where *x* and *y* are charge and multiplicity respectively

The input file was constructed in order to perform sufficient level DFT optimization on stationary computer with following hardware and software: 8 GB RAM, Intel® Core™ i7-4790 CPU @ 3.60 GHz, SDD Sata III Intenso hard drive, Windows 10, 64 bit. We want to stress out that on this level of theory it is not enough to compute accurate molecular orbitals.

3. Structure of optimized PrP^C-Cu(II) a model complex:

atom	x [Å]	y [Å]	z [Å]
Cu	0.5460	0.3445	0.2608
С	2.7262	-1.5397	-0.7909
С	2.8445	0.2556	1.9790
С	3.7412	-0.8760	1.5171
С	0.4854	-1.6079	-1.6960
С	-0.9030	-0.9928	-1.7118
С	-2.1613	0.8483	-0.6189
С	-1.7072	2.0844	0.1664
С	0.1707	3.0550	1.4019
С	-0.2099	2.9000	2.9284
Н	0.7355	-2.3930	-2.4375
Н	-2.5772	1.1569	-1.6067
Н	-2.9983	0.3733	-0.0510
Н	1.2811	2.9856	1.3597
Н	-0.1814	4.0478	1.0407
Н	-0.1080	0.2067	2.8558
Н	-0.6567	-1.2598	2.4968
Ν	1.3188	-1.1459	-0.8353
Ν	-1.0196	-0.0146	-0.7482
Ν	-0.3673	2.0134	0.5930
Ν	-0.6512	4.0103	3.5331
Ν	4.9799	-0.9247	1.9312
0	2.2344	0.8939	0.9131
0	-1.7972	-1.3166	-2.4800
0	-2.4155	3.0358	0.4462
0	-0.0549	1.8113	3.4961
0	0.0337	-0.5975	2.2670
н	5.3649	-0.2030	2.5645
Н	-0.8152	4.8885	3.0296
С	3.2226	-1.9664	0.6212

Н	3.3225	-0.6826	-1.1734
Н	2.8822	-2.3943	-1.4855
Н	2.3869	-2.4661	1.1659
Н	4.0122	-2.7353	0.4787
н	2.1137	-0.2159	2.6942
Н	3.4383	0.9957	2.5739
н	-0.8995	3.9723	4.5313
н	5.6257	-1.6891	1.6698

The optimised PrP^c-Cu(II) **a** model complex was based on structure reported before ⁵. This structure was smaller due to computational limitations. In comparison to previous geometry oxygen ligand has moved significantly, which resulted in reduction of distortion of planar geometry. Nevertheless, the geometrical divergence from planar geometry of Cu²⁺ binding site leads to creation of pre-edge structure.

4. Structure of optimized PrPC-Cu(II) b model complex:

atom	x [Å]	y [Å]	z [Å]
Cu	-1.1644	0.7543	0.2966
0	-2.1521	-0.7615	-0.8184
0	0.1555	-0.7511	1.3099
С	-0.2674	2.6070	2.5641
Ν	-0.5284	2.4760	1.1923
Ν	0.1161	3.8447	2.9421
С	-0.3019	3.6970	0.6953
С	0.1074	4.5622	1.8188
С	-2.7243	-0.4251	2.6737
Ν	-3.8702	-0.4070	3.3915
Ν	-2.6538	0.5496	1.6709
С	-4.5789	0.5943	2.8726
С	-3.8112	1.2139	1.7723
Ν	-0.0666	1.0785	-1.3671
С	1.2307	0.9431	-1.4990
С	-0.5671	1.3869	-2.7128
Ν	1.7379	1.1236	-2.7868
С	0.6937	1.3881	-3.5246
Н	1.0059	-0.7515	1.8040
Н	-0.3639	1.7623	3.2639
Н	-0.4101	3.9527	-0.3691
Н	0.3777	5.6305	1.7835
Н	-1.8966	-1.1292	2.8483
Н	-5.5786	0.8802	3.2394
Н	-4.0895	2.0592	1.1240
Н	1.9014	0.6960	-0.6599
Н	-1.1025	2.3665	-2.7424
Н	0.7709	1.5863	-4.6089

С	-2.1618	-1.9951	-0.8868
Н	-1.3077	0.6237	-3.0506
С	-3.0899	-2.7721	-1.7760
0	-1.2917	-2.6863	-0.1194
Н	0.0088	-1.6619	0.9524
Н	-1.3701	-3.6660	-0.2394
Н	-2.5122	-3.3995	-2.4936
Н	-3.7472	-2.0834	-2.3410
Н	-3.7241	-3.4590	-1.1688

The optimised PrP^c-Cu(II) **a** model complex was based on structure reported before ⁵. In this case, one of imidazole ligands was replaced by carbonyl group, which significantly increased stability of convergence of SCF.

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