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Electronic Supporting Information for

Mechanism of the S_1 Excited State Internal Conversion in Vitamin B_{12}

Piotr Lodowski,[1] Maria Jaworska,[1] Tadeusz Andruniów,[2] Brady D. Garabato,[3] and Pawel M. Kozlowski[3]

[1] Department of Theoretical Chemistry, Institute of Chemistry,
University of Silesia, Szkolna 9, PL-40 006 Katowice, Poland,

[2] Institute of Physical and Theoretical Chemistry, Department of Chemistry,
Wroclaw University of Technology, 50-370 Wroclaw, Poland.

[3] Department of Chemistry, University of Louisville, Louisville, Kentucky 40292, USA.

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References

Computational Details

In accordance with the previous computational studies, a Im-[Co^{III}(corrin)]-CN^+ truncated model of vitamin B_{12} was used in all calculations. The high-resolution X-ray crystallographic data for structure of CNCbl[1] was the source used to prepare the employed structural model. In the model all side chains of the corrin ring and the nucleotide loop were replaced by hydrogen atoms and the 5,6-dimethylbenzimidazole *trans* axial base was replaced by an imidazole. Since the nucleotide side chain containing the negatively charged $PO4^-$ group has been truncated, the resulting Im-[Co^{III}(corrin)]-CN^+ structural model of CNCbl has a total charge of +1.

All of the calculations were carried out using DFT and TD-DFT methods with the gradient-corrected Becke-Perdew (BP86) functional. The basis set used for geometry optimization, and PES, were TZVPP for all atoms except hydrogen which was described by the TZVP basis set. These basis sets are of the form: (17s11p6d1f)/[6s4p3d1f] for Co, (11s6p2d1f)/[5s3p2d1f] for N, C and (5s1p)/[3s1p] for H atoms. To reduce the computational cost of calculations, the Resolution of the Identity approach for computing the electronic coulomb interaction (RI-J) was applied with the corresponding auxiliary basis sets for RI-DFT. The effect of environment was taken into account by COSMO solvent model in all calculations with water as solvent.

Table S1. Selected bond lengths (Å), bond angles and dihedral angles (degrees) of Im-[Co^{III}(corrin)]-CN^+ compared with experimental data for CNCbl.

Structural parameter	S_0	Exp. [a]		S_1
		CNCbl(LiCl)	CNCbl(KCl)	
r [Å]				
Co-C_{CN}	1.857	1.886	1.867	2.216
C-N_{Im}(N_{DMB})	2.054	2.041	2.029	2.275
Co-N_{21}	1.894	1.881	1.864	1.884
Co-N_{22}	1.947	1.910	1.903	1.949
Co-N_{23}	1.947	1.920	1.907	1.950
Co-N_{24}	1.892	1.883	1.896	1.874
C_{CN}-N_{CN}	1.172	1.161	1.136	1.175
Bond angles [deg]				
C_{CN}-Co-N_{Im}(N_{DMB})	178.6	177.9	174.7	177.1
Co-C_{CN}-N_{CN}	179.6	178.2	175.6	170.4
N_{21}-Co-C_{CN}	92.1	90.6	91.4	91.9
N_{22}-Co-C_{CN}	88.1	88.4	87.7	87.5
N_{23}-Co-C_{CN}	90.8	91.0	89.7	92.3
N_{24}-Co-C_{CN}	88.6	86.6	88.8	88.8
Torsion angles [deg]				
N_{21}-N_{22}-N_{23}-Co	-1.9	-1.0	-0.5	-2.7
N_{21}-N_{22}-N_{23}-N_{24}	-4.1	-4.4	-3.0	-5.1
Co-N_{22}-C_9-C_{10}	1.4	-7.9	-13.6	2.2
Co-N_{22}-C_6-C_5	-6.9	-18.8	-11.2	-5.6
Co-N_{23}-C_{14}-C_{15}	-0.6	-1.0	0.1	-5.2
Co-N_{21}-C_1-C_{19}	33.1	33.4	33.5	32.4

[a] The experimental values based on high-resolution X-ray crystal structures from Ref. 1

Table S2. NBO charges for Im-[Co^{III}(corrin)]-CN^+ in S_0 and S_1 optimized geometry.

	NBO charges			
	S_0	S_1		
	q_{S0}	q_{S0}	q_{S1}	Δq [a)]
Co	0.691	0.851	0.832	-0.019
C_{CN}	0.147	0.083	-0.075	-0.159
N_{Im}	-0.454	-0.437	-0.491	-0.054
CN	-0.431	-0.495	-0.726	-0.231
Im	0.242	0.240	0.127	-0.113
Corr	0.499	0.404	0.766	0.362

[a)] Δq – difference between the charge in the excited state and ground state in the geometry excited state.

Table S3. The ten lowest, vertical singlet electronic transitions for Im-[Co^{III}(corrin)]-CN^+ model complex based on the TD-DFT calculations.

	E(eV)	λ(nm)	*f*	%	character			Exp.[a] nm (eV)
S_1	2.49	497.9	0.0471	87	119 → 120	H → L	$\pi \rightarrow \pi*$	550(2.25)
S_2	2.59	478.6	0.0076	80	119 → 121	H → L+1	$\pi \rightarrow d_{xy}$+n	517(2.40)
S_3	2.66	466.3	0.0168	47	119 → 122	H → L+2	$\pi \rightarrow \sigma*(d_{z2})$ +n	
				42	118 → 120	H-1 → L	$\pi+d_{yz} \rightarrow \pi^*$	
S_4	2.73	454.5	0.0183	50	119 → 122	H → L+2	$\pi \rightarrow \sigma^*(d_{z2})$ +n	485(2.56)
				28	118 → 120	H-1 → L	$\pi+d_{yz} \rightarrow \pi^*$	
S_5	2.79	444.7	0.0036	75	118 → 121	H-1 → L+1	$\pi+d_{yz} \rightarrow d_{xy}$+n	
S_6	2.87	431.5	0.0062	40	117 → 120	H-2 → L	$d_{xz} \rightarrow \pi^*$	
				39	118 → 122	H-1 → L+2	$\pi+d_{yz} \rightarrow \sigma^*(d_{z2})$ +n	
S_7	2.91	426.6	0.0281	44	117 → 120	H-2 → L	$d_{xz} \rightarrow \pi^*$	457(2.71)
				40	118 → 122	H-1 → L+2	$\pi+d_{yz} \rightarrow \sigma^*(d_{z2})$ +n	
S_8	3.05	406.7	0.0000	96	116 → 120	H-3 → L	$d_{x2-y2} \rightarrow \pi^*$	
S_9	3.10	399.5	0.0069	92	115 → 120	H-4 → L	$\pi_{Im} \rightarrow \pi^*$	
S_{10}	3.26	379.7	0.0010	61	117 → 121	H-2 → L+1	$d_{xz} \rightarrow d_{xy}$+n	
				25	117 → 122	H-2 → L+2	$d_{xz} \rightarrow \sigma^*(d_{z2})$ +n	

[a)] The experimental data from Ref. 2

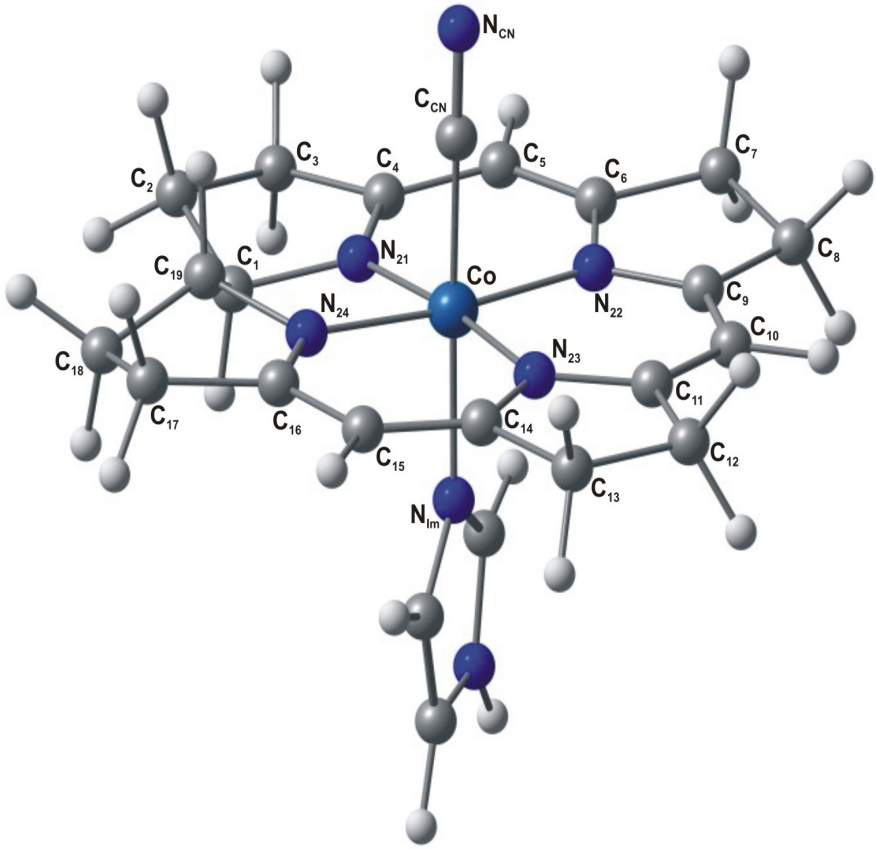

Figure S1. Structural model of CNCbl used in the calculations.

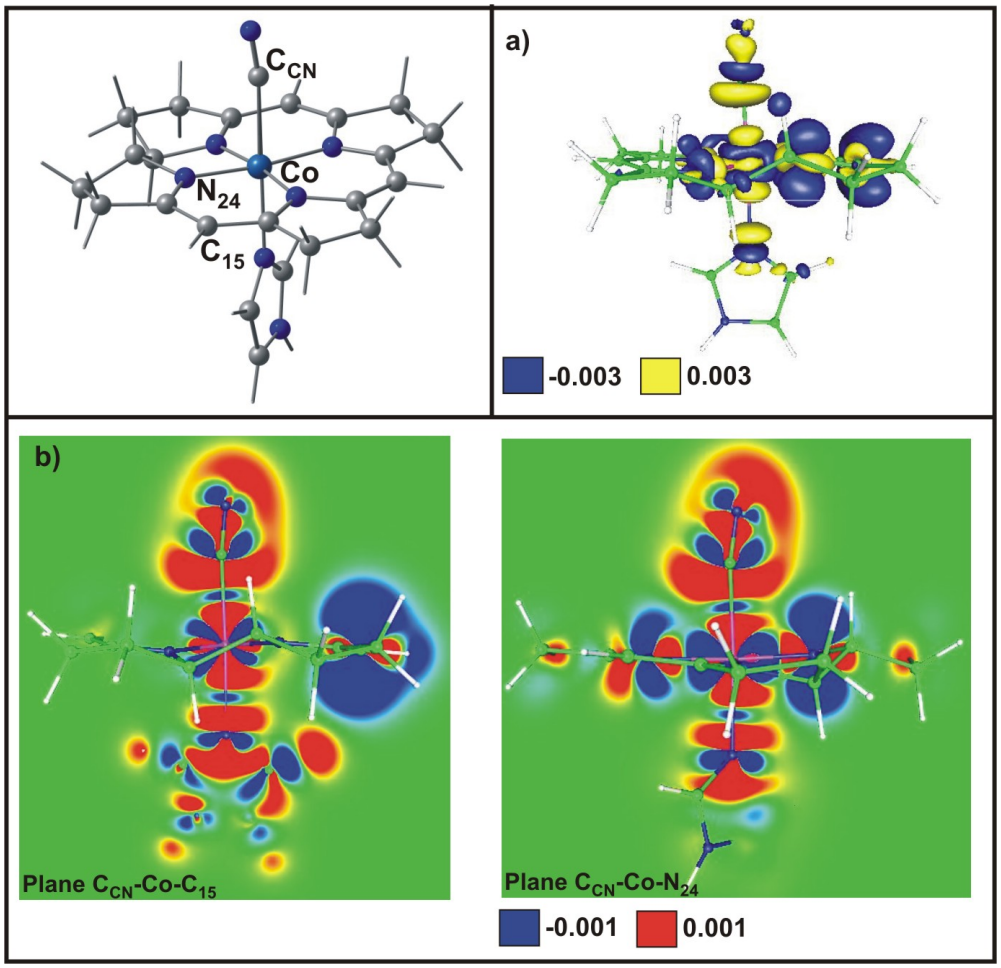

Figure S2. Electron density difference between the S_1 and S_0 states for the S_1 optimized geometry of CNCbl model (Im-[Co^{III}(corrin)]-CN^+) : (a) isosurface plot value of 0.003 and (b) cross-section contour plot along the axial bonding at two planes penperdicular to the corrin ring. The yellow and red colors denote electron space. Blue color = hole space.

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