Insights into the Electronic Structure of Copper(II) Bound to an Imidazole Analogue of Westiellamide

Supporting Information

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Table S1. Calculated g and $A(^{63}Cu)$ matrices for $[Cu^{II}(H_2L^2)(MeOH)_2]^+$ with various combinations of functionals and basis sets. The Wachters[1] basis set was solely applied to copper.

	g-values			A(^{63}Cu) values [10^{-4} cm^{-1}]		
	g_x	g_y	g_z	$\|A_x\|$	$\|A_y\|$	$\|A_z\|$
Experimental values[2]	2.083	2.034	2.279	15	17	153
Functional / Basis set						
MAG-ReSpect[3]	2.081	2.095	2.292	19	4	182
BHLYP / TZVP[4] Wachters	2.092	2.102	2.319	9	31	314
BHLYP / IGLO-II[5] Wachters	2.081	2.101	2.305	1	17	298
BHLYP / EPR-II[6] Wachters	2.060	2.142	2.304	21	72	305
BHLYP / 6-311g*[7] Wachters	2.085	2.100	2.304	11	33	311
B40LYP / IGLO-II[5] Wachters	2.086	2.097	2.302	21	72	305
BHLYP / IGLO-II[5] Wachters SOC	2.061	2.143	2.305	15	66	291

Table S2. Calculated g and $A(^{63}Cu)$ matrices for $[Cu^{II}(H_2L^3)(MeOH)_2]^+$ with various combinations of functionals and basis sets. The Wachters[1] basis set was solely applied to copper.

	g values			A(^{63}Cu) values [10^{-4} cm^{-1}]		
	g_x	g_y	g_z	$\|A_x\|$	$\|A_y\|$	$\|A_z\|$
Experimental values[2]	2.082	2.037	2.263	15	19	150
Functional / Basis set						
MAG-ReSpect[3]	2.082	2.096	2.295	35	25	166
B38LYP / IGLO-II[5] Wachters	2.070	2.083	2.244	9	28	289
B38LYP / IGLO-II[5] Bauschlicher	2.071	2.085	2.257	100	120	175
BHLYP / 6-311g*[7] IGLO-II Wachters	2.088	2.099	2.305	11	31	311
BHLYP / 6-311g*[7] Wachters	2.081	2.102	2.306	18	18	298
BHLYP / EPR II[6] Wachters	2.087	2.099	2,302	109	31	310
BHLYP / IGLO-II[5] Wachters	2.081	2.101	2.305	2	17	298
BHLYP / IGLO-II[5] grid5	2.086	2.099	2.302	10	31	310
BHLYP / IGLO-II[5] grid5 SCF tight	2.086	2.099	2.302	11	31	311
BHLYP / IGLO-II[5] Kaupp	2.089	2.100	2.309	12	31	305
BHLYP / IGLO-II[5] SOCFlag 1,3,3,5	2.086	2.099	2.302	10	31	310
BHLYP / TZV[4] Wachters	2.086	2.109	2.322	2	15	300
BHLYP / TZV[4] IGLO-II[5] Wachters	2.088	2.099	2.306	10	30	310
BHLYP / TZVP[4] Wachters	2.086	2.109	2.322	3	15	300
BHLYP / IGLO-II[5] Wachters	2.086	2.099	2.302	11	31	310
BHLYP / IGLO-II[5] Wachters SOC	2.086	2.098	2.300	12	30	176

Table S3. Calculated g and $A(^{63}Cu)$ matrices for $[Cu^{II}(H_2L^{wa})(MeOH)_2]^+$ with various combinations of functionals and basis sets. The Wachters[1] basis set was solely applied to copper.

	g values			A(^{63}Cu) values [10^{-4} cm^{-1}]		
	g_x	g_y	g_z	$\|A_x\|$	$\|A_y\|$	$\|A_z\|$
Experimental values[2]	2.083	2.051	2.267	14	16	175
Functional / Basis set						
BHLYP / EPR-II[6] Wachters	2,072	2,097	2,298	0	35	303
BHLYP / IGLO-II[5] Wachters	2,091	2,101	2,324	8	16	302
BHLYP / IGLO-II[5] Partridge	2,095	2,110	2,344	0	13	296
MAG-ReSpect[3] BHLYP IGLO-II[5]	2,090	2,094	2,311	not determined		

Table S4. Calculated $A(^{14}N)$ matrices for the ligating nitrogen atoms in $[Cu^{II}(H_2L^1)(MeOH)_2]^+$.

Method & Nucleus	A_x[a]	A_y[a]	A_z[a]	A_{iso}[a]	P[a]	η
Experimental values (Pulsed EPR)						
N (Im) : N-3	14.00	11.50	12.70	12.73	-3.2	0.62
N (Amide) : N-4	13.80	14.30	12.70	13.60	-2.0	0.40
N (Im) : N-5	14.00	11.50	12.70	12.73	-3.2	0.62
BHLYP-IGLOOII-TZVP (Orca)						
N (Im) : N-3	10.12	10.23	12.84	11.06	-2.314	0.869
N (Amide) : N-4	11.70	12.09	16.20	13.33	3.352	0.638
N (Im) : N-5	10.85	11.06	13.32	11.74	-2.454	0.673
MAG-ReSpect BHLYP IGLO-II						
N (Im) : N-3	10.60	10.70	13.45	11.58	-[b]	-[b]
N (Amide) : N-4	12.68	13.08	17.61	14.46	-[b]	-[b]
N (Im) : N-5	11.38	11.60	13.93	12.30	-[b]	-[b]

[a] Units for hyperfine and quadrupole couplings are10^{-4} cm^{-1}. [b] Not calculated.

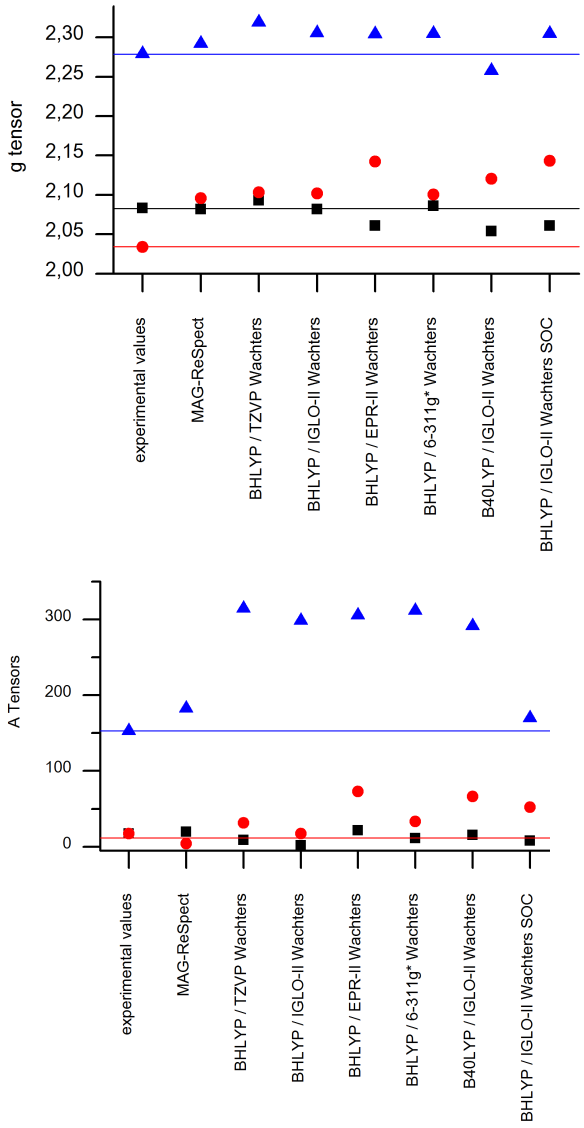


Figure S1. Calculated and experimental[2] (a) g and (b) $|A|(^{63}Cu)$ matrices for the copper(II) complex of H_3L^2, ($[Cu^{II}(H_2L^2)(MeOH)_2]^+$) calculated with various combinations of functionals and basis sets with the program packages ORCA[8] and MAG-ReSpect.[3] The experimental values are depicted as horizontal lines.

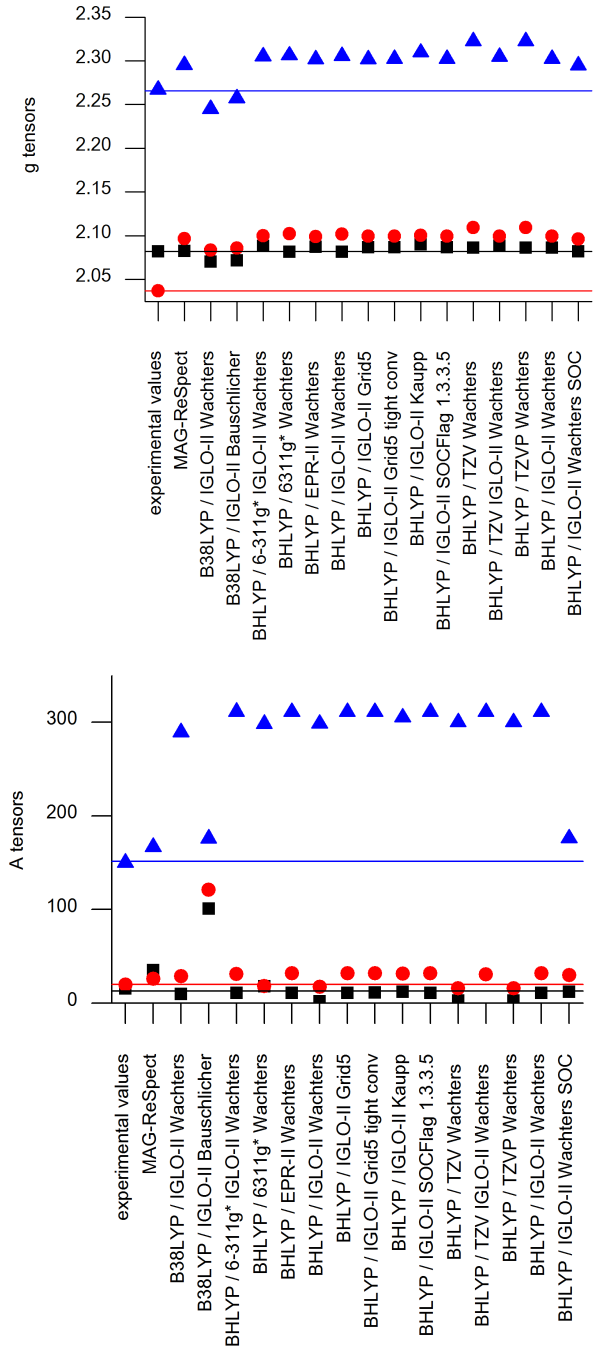
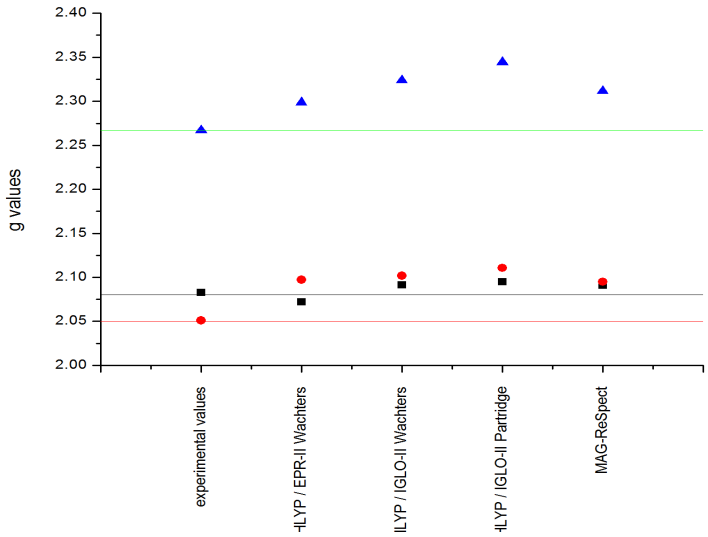


Figure S2. Calculated and experimental[2] (a) g and (b) $|A|(^{63}Cu)$ matrices for the copper(II) complex of H_3L^3, ($[Cu^{II}(H_2L^3)(MeOH)_2]^+$) calculated with various combinations of functionals and basis sets with the program packages ORCA[8] and MAG-ReSpect.[3] The experimental values are depicted as horizontal lines.

(a)



(b)

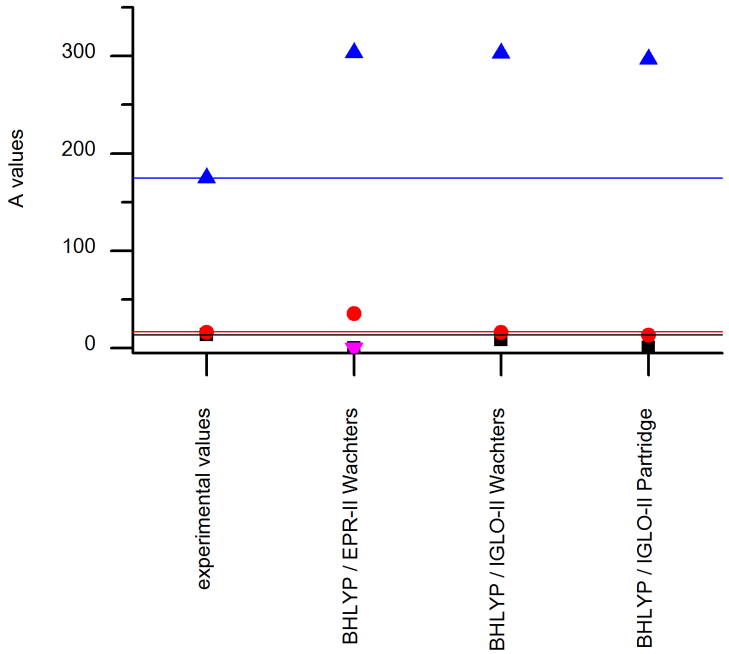


Figure S3. Calculated and experimental[2] (a) g and (b) $|A|(^{63}Cu)$ matrices for the copper(II) complex of H_3L^{wa}, ($[Cu^{II}(H_2L^{wa})(MeOH)_2]^+$) calculated with various combinations of functionals and basis sets with the program packages ORCA[8] and MAG-ReSpect.[3] The experimental values are depicted as horizontal lines.

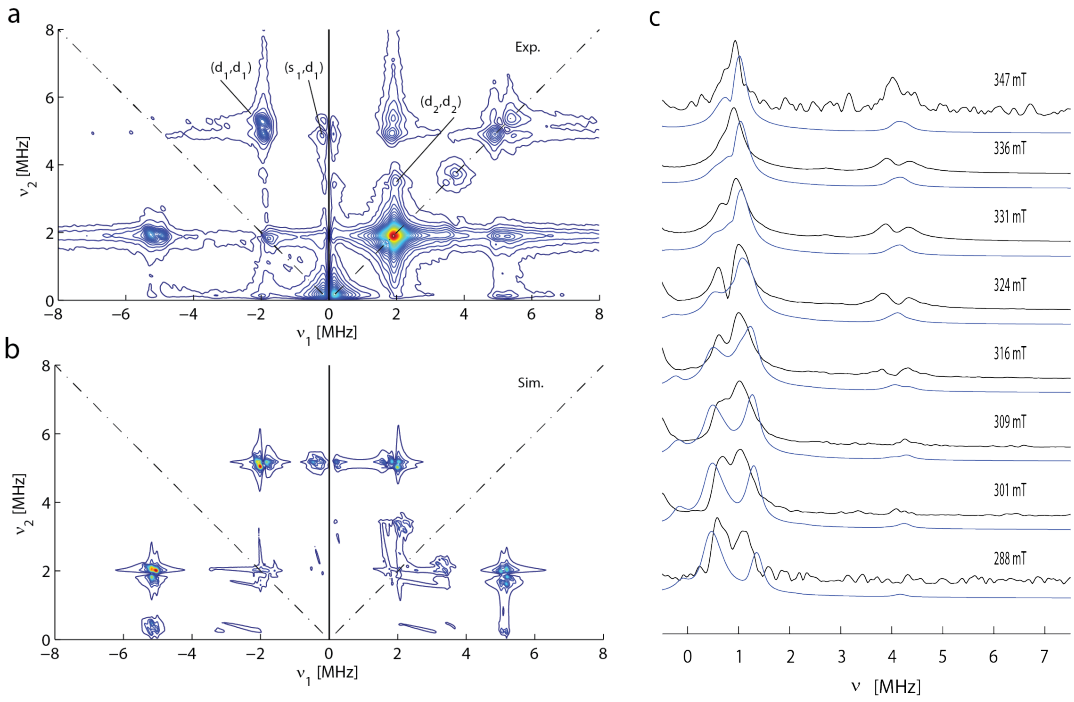


Figure S4. HYSCORE and 3-pulse ESEEM spectra of $[Cu^{II}(H_2L^1)(MeOH)_2]^+$ in methanol. (a) X-band (ν = 9.671 GHz) HYSCORE spectrum recorded at 335.0 mT and 5.0 K. ^{14}N single- and double-quantum cross peaks are labeled s and d, respectively. A selection of cross-peaks are labeled for two nuclei which are identified by the subscript, for reference the nitrogen Larmor frequency is ν(^{14}N) = 1.03 MHz. (b) Computer simulation of (a). (c) X-band (ν = 9.671 GHz) three-pulse ESEEM spectra recorded at 5.0 K at the indicated field positions (black) along with the simulations (blue) for a remote nitrogen. Computer simulation of the HYSCORE and orientation selective 3-pulse ESEEM spectra assumed coupling to two different ^{14}N nuclei. Spin Hamiltonian parameters for these nuclei are: $A_{x,y,z}$ (^{14}N-14) = 2.5, 2.6, 3.0 MHz; α, β, γ = 20, 0, 0; P (^{14}N-14) = -2.4 MHz, η = 0.2; $A_{x,y,z}$ (^{14}N-34) = 0.6, 0.6, 1.0 MHz; α, β, γ = -20, 0, 0; P (^{14}N-14) = -2.2 MHz, η = 0.1. Clearly, the simulations assuming two different ^{14}N nuclei do not account for the double peaks in both the HYSCORE and orientation selective 3-pulse ESEEM spectra.

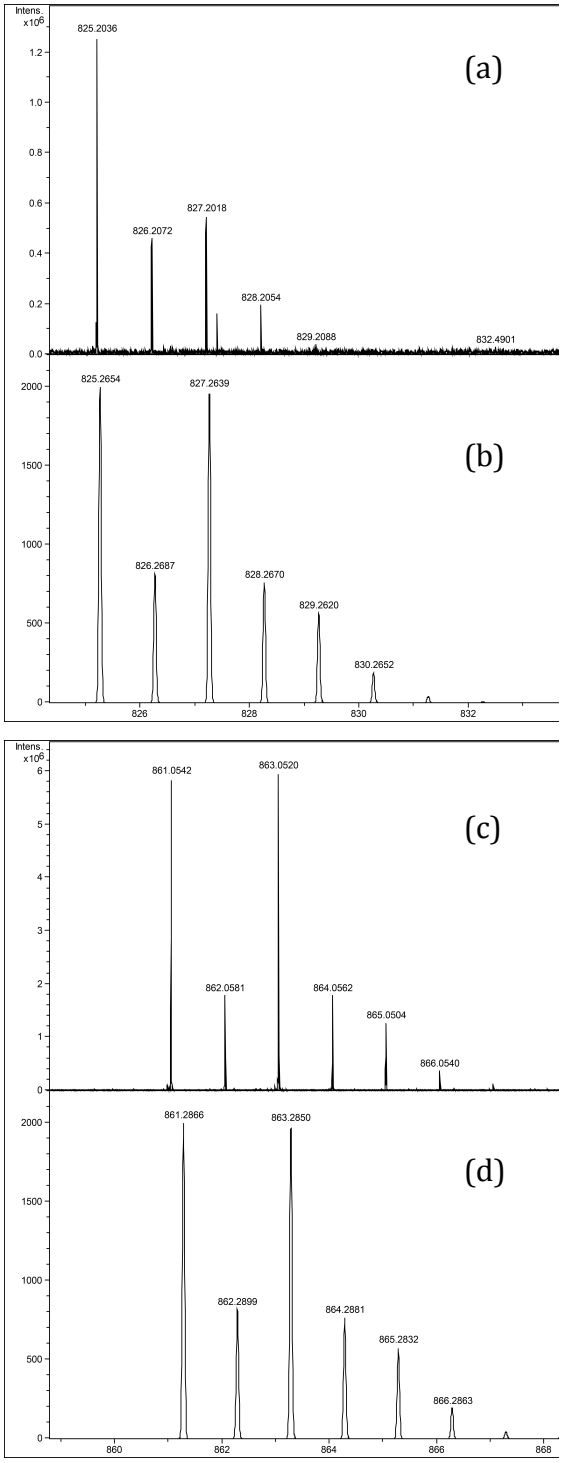


Figure S5. Mass Spectra of the dinuclear Cu^{II} complex of H_3L^1 in a 50:50 methanol: glycerol solution. (a) Experimental spectrum showing the m/z = 825.20358 peak, (b) Calculated spectrum for $[Cu_2HL^1(OCH(CH_2OH)_2)MeOH]^+$, m/z=825.26545, (c) Experimental spectrum showing the m/z=861.05422 peak, (d) Calculated spectrum for $[Cu_2L^1(OCH(CH_2OH)_2)MeOH(H_2O)]^+$ (m/z= 861.28658).

Supporting Information References

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