SupplementaryMaterial

(Total of 33 pages)

X-ray structure and density functional theory studies of an unexpected product *trans*-bis{2-[(2-cyanoethyl)iminomethyl] phenolato}copper(II)

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Details on levels of theory used for calculations.

All structures were fully optimised (unless otherwise specified) using B3LYP methods and different levels of theory (Frisch & Frisch, 1998) for comparative purposes. The free ligands, $CYMB^-$ and $TIMB^-$, were calculated at the Lanl2dz (BS1), 6-31G** (BS2) and 6-311++G** (BS3) levels for all atoms. The copper complexes, $[Cu^{I/II}(CYMB)_2]^{-/0}$ and $[Cu^{I/II}(TIMB)_2]^{-/0}$, were calculated at the Lanl2dz(CuCHNOF) (BS4), Lanl2dz(CuF);6-31G**(CHNO) (BS5) and Lanl2dz(CuF);6-311++G**(CHNO) (BS6) levels (Frisch & Frisch, 1998). The input structures for both copper(II) complexes were from experimental X-ray data (complex (I) from this study and the analogous data for complex (II), $[Cu^{II}(DIMB)_2]$, having CH_3 groups instead of CF_3; see Corsini et al., 2003). Single-point calculations were performed at the BS4 and BS5 levels of theory in order to estimate the Mulliken atomic charge (e) and the total electronic energies (Hartrees). The optimised structures of complexes $[Cu^{II}(CYMB)_2]$ and $[Cu^{II}(TIMB)_2]$ were used as input for the computation of $[Cu^{I}(CYMB)_2]^-$ at the BS4 and BS5 levels and $[Cu^{I}(TIMB)_2]^-$ at the BS4 level of theory.

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Table S19. Selected geometrical parameters (bond distances and bond angles) for the fully optimized structures $TIMB^-$ free-ligand and $[Cu^{II}(TIMB)_2]$ and $[Cu^{I}(TIMB)_2]^-$ complexes, at

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Table S20. Mulliken atomic charges (e) for fully optimized structures $CYMB^-$ and $TIMB^-$ free-ligands, and $[Cu^{I/II}(CYMB)_2]^{-/0}$ and $[Cu^{I/II}(TIMB)_2]^{-/0}$ complexes, at different levels of theory (see text for details). Values from single point (SP) calculation for copper(II) complexes from X-ray structures have been included for comparative purposes.

Figure S1. Crystal packing of (**I**) as viewed almost along the (a) **a** cell edge and (b) **b** cell edge.

Table S1. Computed Cartesian coordinates (in Å) of $CYMB^-$ free-ligand at B3LYP/BS1 level of theory.

Atom	**x**	**y**	**z**
O	1.175958	2.114409	.492754
N	-1.221138	.672225	-.653481
N	-3.996724	-1.431255	1.537061
C	1.837455	-1.407571	-.499827
H	1.314661	-2.266259	-.930682
C	3.187312	-1.533909	-.167631
H	3.721288	-2.468521	-.329584
C	3.848216	-.399777	.394168
H	4.904465	-.472909	.663189
C	3.167177	.791535	.602274
H	3.669478	1.658499	1.031155
C	1.749647	.979776	.274691
C	1.088884	-.207139	-.304909
C	-.299707	-.260719	-.722672
H	-.576135	-1.246272	-1.160623
C	-2.541927	.359380	-1.201113
H	-2.648857	-.672374	-1.602556
H	-2.759939	1.060277	-2.023449
C	-3.641185	.609884	-.121623
H	-3.333282	1.499416	.442128
H	-4.613766	.813879	-.593468
C	-3.822629	-.516094	.809441

Table S2. Computed Cartesian coordinates (in Å) of $CYMB^-$ free-ligand at B3LYP/BS2 level of theory.

Atom	**x**	**y**	**z**
O	1.109371	2.068938	.473419
N	-1.210739	.643212	-.664000
N	-3.877998	-1.352785	1.613986
C	1.833159	-1.394993	-.495617
H	1.328176	-2.260851	-.929168
C	3.170210	-1.495498	-.157203
H	3.721658	-2.418937	-.314466
C	3.801221	-.356151	.402001
H	4.856230	-.412181	.676191
C	3.110200	.814128	.603519
H	3.597332	1.687501	1.032774
C	1.696910	.983372	.271137
C	1.069614	-.218211	-.309263
C	-.305367	-.278566	-.732292
H	-.580207	-1.258460	-1.178669
C	-2.498043	.322546	-1.212726
H	-2.585656	-.709979	-1.608908
H	-2.726911	1.004697	-2.048126
C	-3.618959	.560454	-.165983
H	-3.399309	1.504448	.343856
H	-4.595959	.656644	-.657739
C	-3.737140	-.499975	.837593

Table S3. Computed Cartesian coordinates (in Å) of $CYMB^-$ free-ligand at B3LYP/BS3 level of theory.

Atom	**x**	**y**	**z**
O	1.127145	2.076768	.419957
N	-1.206544	.589407	-.666729
N	-3.988241	-1.249577	1.638738
C	1.854428	-1.406170	-.448782
H	1.352109	-2.283788	-.854567
C	3.192076	-1.494826	-.110940
H	3.742874	-2.419899	-.242587
C	3.820737	-.340309	.412695
H	4.873749	-.384307	.686541
C	3.127468	.833006	.581709
H	3.614654	1.716548	.984161
C	1.716378	.987393	.248079
C	1.088864	-.227927	-.294951
C	-.288396	-.312479	-.712877
H	-.550670	-1.305150	-1.132862
C	-2.489205	.245974	-1.214412
H	-2.569728	-.808695	-1.541229
H	-2.685690	.874388	-2.095286
C	-3.626786	.563312	-.210707
H	-3.399954	1.524146	.259563
H	-4.584577	.656994	-.735333
C	-3.803304	-.441838	.834833

Table S4. Computed Cartesian coordinates (in Å) of $TIMB^-$ free-ligand at B3LYP/BS1 level of theory.

Atom	**x**	**y**	**z**
H	-7.605513	0.009162	0.139640
H	-6.322483	-1.688553	-1.153768
C	-6.514455	0.015336	0.158053
C	-5.810464	-0.931422	-0.561832
H	-6.396103	1.756556	1.492328
C	-5.832774	1.013404	0.932120
C	-4.342014	-0.982691	-0.597569
O	-3.742422	-1.863567	-1.312779
C	-4.445937	1.003418	0.950555
C	-3.659595	0.041677	0.227346
H	-3.912625	1.752296	1.540852
C	-2.242337	0.153657	0.367727
H	-1.928958	1.013283	0.993182
N	-1.302615	-0.656094	-0.104855
H	-0.142307	1.839132	-0.294337
C	0.035482	-0.319436	-0.050420
C	0.547786	1.012366	-0.156766
H	0.604962	-2.391996	0.082118
C	0.989489	-1.378226	0.040873
C	1.932436	1.249722	-0.144318
C	2.432931	2.658278	-0.216022
C	2.361887	-1.112771	0.055280
C	2.864425	0.204592	-0.029258
H	3.930505	0.398789	-0.043724
C	3.335550	-2.237663	0.210215
F	4.543096	-2.022930	-0.488166
F	3.734631	-2.450705	1.557043
F	2.846611	-3.476421	-0.227843
F	2.541606	3.279861	1.056553
F	3.719270	2.766114	-0.779928
F	1.605424	3.511980	-0.966101

Table S5. Computed Cartesian coordinates (in Å) of $TIMB^-$ free-ligand at B3LYP/BS2 level of theory.

Atom	**x**	**y**	**z**
H	-7.528086	0.026264	0.204969
H	-6.300236	-1.660407	-1.116015
C	-6.439542	0.024602	0.202715
C	-5.767309	-0.915750	-0.532445
H	-6.286674	1.745202	1.541532
C	-5.743446	1.003462	0.965802
C	-4.307679	-0.982568	-0.599526
O	-3.734919	-1.839507	-1.301868
C	-4.367878	0.982734	0.955610
C	-3.609996	0.031094	0.217317
H	-3.819377	1.721867	1.538224
C	-2.195820	0.132835	0.321495
H	-1.859122	0.979000	0.946047
N	-1.290075	-0.663505	-0.181493
H	-0.151737	1.814867	-0.350940
C	0.034312	-0.327531	-0.105120
C	0.538044	0.993680	-0.200235
H	0.611877	-2.389918	0.028200
C	0.984790	-1.373612	-0.005025
C	1.909688	1.239474	-0.159811
C	2.399279	2.655870	-0.206777
C	2.344989	-1.103893	0.038896
C	2.835803	0.206415	-0.026635
H	3.898623	0.405156	-0.016310
C	3.322351	-2.224775	0.225612
F	4.506688	-2.006793	-0.427615
F	3.662233	-2.410955	1.543619
F	2.856435	-3.427518	-0.212599
F	2.426279	3.244430	1.033639
F	3.673664	2.764248	-0.692392
F	1.621266	3.466181	-0.982602

Table S6. Computed Cartesian coordinates (in Å) of $TIMB^-$ free-ligand at B3LYP/BS3 level of theory.

Atom	**x**	**y**	**z**
H	-7.517238	0.025804	0.248406
H	-6.312134	-1.619363	-1.139746
C	-6.428980	0.020179	0.234327
C	-5.769302	-0.897117	-0.537443
H	-6.255691	1.694855	1.625807
C	-5.721643	0.970629	1.020555
C	-4.311890	-0.968737	-0.623184
O	-3.751057	-1.801077	-1.360612
C	-4.347247	0.945137	0.994108
C	-3.601635	0.015928	0.217071
H	-3.789090	1.662892	1.593365
C	-2.185565	0.110568	0.311953
H	-1.843649	0.944371	0.950480
N	-1.284446	-0.674659	-0.210483
H	-0.155546	1.802827	-0.370766
C	0.039915	-0.336612	-0.130857
C	0.537738	0.985239	-0.219691
H	0.625349	-2.395209	0.008094
C	0.993973	-1.377903	-0.024704
C	1.907815	1.237984	-0.168398
C	2.380981	2.657345	-0.206869
C	2.351637	-1.102531	0.031969
C	2.836760	0.209978	-0.029912
H	3.897222	0.414423	-0.006386
C	3.329498	-2.216673	0.233705
F	4.524730	-1.998023	-0.406624
F	3.656250	-2.398064	1.559667
F	2.875356	-3.427559	-0.204902
F	2.256702	3.287801	1.010554
F	3.702201	2.777900	-0.550314
F	1.682319	3.433516	-1.093578

Table S7. Computed Cartesian coordinates (in Å) of $[Cu^{II}(CYMB)_2]$ complex at B3LYP/BS4 level of theory.

Atom	x	y	z
Cu	.000056	-.000068	-.000079
O	1.484442	1.217233	.275538
N	1.263776	-1.433281	-.686512
N	2.508548	-4.471929	1.348930
C	4.793702	-.282590	-.508906
H	5.212343	-1.216062	-.882727
C	5.637308	.770879	-.167296
H	6.714042	.676026	-.270775
C	5.066488	1.975542	.324156
H	5.715317	2.805864	.595320
C	3.685190	2.110183	.467198
H	3.247670	3.029487	.846617
C	2.802431	1.041674	.125641
C	3.377235	-.175671	-.373050
C	2.573612	-1.307556	-.754147
H	3.140529	-2.158618	-1.149483
C	.692561	-2.723891	-1.146585
H	1.393233	-3.228866	-1.827192
H	-.240269	-2.516099	-1.671485
C	.346757	-3.660878	.042351
H	-.331966	-3.127698	.715889
H	-.189475	-4.538995	-.341446
C	1.538951	-4.117025	.775866
O	-1.484389	-1.217258	-.275898
N	-1.263593	1.433087	.686557
N	-2.509254	4.472214	-1.347601
C	-4.793582	.282611	.508738
H	-5.212180	1.216043	.882709
C	-5.637240	-.770754	.166937
H	-6.713971	-.675861	.270416
C	-5.066477	-1.975365	-.324708
H	-5.715347	-2.805605	-.596024
C	-3.685183	-2.110056	-.467748
H	-3.247707	-3.029319	-.847318
C	-2.802372	-1.041652	-.126000
C	-3.377119	.175638	.372891
C	-2.573436	1.307413	.754189
H	-3.140311	2.158449	1.149640
C	-.692288	2.723602	1.146800
H	-1.392777	3.228353	1.827758
H	.240724	2.515742	1.671353
C	-.346960	3.660952	-.041984
H	.331568	3.127991	-.715894
H	.189351	4.538993	.341877
C	-1.539437	4.117230	-.774958

Table S8. Computed Cartesian coordinates (in Å) of $[Cu^{II}(CYMB)_2]$ complex at B3LYP/BS5 level of theory.

Atom	**x**	**y**	**z**
Cu	.000018	-.000020	-.000056
O	1.483078	1.203054	.302141
N	1.271847	-1.446340	-.686177
N	2.461622	-4.419292	1.383523
C	4.750356	-.266673	-.518725
H	5.166806	-1.192678	-.904881
C	5.586332	.775840	-.179004
H	6.659770	.685355	-.294101
C	5.017018	1.961143	.325292
H	5.661325	2.790887	.599208
C	3.650152	2.088589	.481523
H	3.216023	3.001512	.873843
C	2.765831	1.030660	.141107
C	3.345073	-.170711	-.370538
C	2.559962	-1.303797	-.754217
H	3.136454	-2.143489	-1.154659
C	.726467	-2.724555	-1.146155
H	1.447362	-3.229612	-1.798421
H	-.186770	-2.529582	-1.706533
C	.351589	-3.653316	.027759
H	-.352622	-3.134185	.682439
H	-.155777	-4.540717	-.365146
C	1.518265	-4.087002	.797706
O	-1.483056	-1.203029	-.302440
N	-1.271793	1.446209	.686286
N	-2.461826	4.419512	-1.382752
C	-4.750321	.266628	.518601
H	-5.166761	1.192577	.904903
C	-5.586311	-.775812	.178690
H	-6.659749	-.685326	.293782
C	-5.017010	-1.961043	-.325794
H	-5.661329	-2.790727	-.599863
C	-3.650144	-2.088489	-.482019
H	-3.216025	-3.001353	-.874486
C	-2.765810	-1.030633	-.141410
C	-3.345038	.170664	.370422
C	-2.559911	1.303672	.754298
H	-3.136394	2.143307	1.154874
C	-.726403	2.724352	1.146458
H	-1.447253	3.229269	1.798883
H	.186885	2.529295	1.706724
C	-.351655	3.653358	-.027305
H	.352530	3.134384	-.682136
H	.155696	4.540706	.365739
C	-1.518409	4.087147	-.797074

Table S9. Computed Cartesian coordinates (in Å) of $[Cu^{II}(CYMB)_2]$ complex at B3LYP/BS6 level of theory.

Atom	**x**	**y**	**z**
Cu	.000052	.000236	.000062
O	1.489367	1.205990	.309935
N	1.274162	-1.441526	-.692767
N	2.494372	-4.343361	1.410547
C	4.750646	-.254846	-.543962
H	5.164172	-1.174771	-.946133
C	5.588206	.780767	-.192159
H	6.660506	.691855	-.313978
C	5.022709	1.956545	.335406
H	5.669095	2.780425	.620489
C	3.658109	2.082313	.500164
H	3.227876	2.988756	.910113
C	2.770772	1.032653	.144650
C	3.346463	-.161044	-.387760
C	2.559613	-1.292778	-.773350
H	3.136525	-2.127652	-1.182566
C	.732475	-2.726611	-1.143803
H	1.451096	-3.224837	-1.803089
H	-.186939	-2.539241	-1.694583
C	.379674	-3.655578	.036822
H	-.345950	-3.154959	.681077
H	-.097016	-4.561472	-.350648
C	1.550254	-4.045764	.818391
O	-1.488966	-1.205747	-.310136
N	-1.274462	1.441694	.693134
N	-2.494269	4.343006	-1.410714
C	-4.750665	.254295	.543499
H	-5.164443	1.174059	.945780
C	-5.587957	-.781421	.191364
H	-6.660295	-.692748	.313026
C	-5.022137	-1.956987	-.336331
H	-5.668310	-2.780943	-.621678
C	-3.657486	-2.082452	-.500885
H	-3.226994	-2.988726	-.910937
C	-2.770422	-1.032682	-.145024
C	-3.346437	.160810	.387501
C	-2.559887	1.292628	.773468
H	-3.137031	2.127272	1.182825
C	-.733383	2.726854	1.144706
H	-1.452629	3.224743	1.803563
H	.185698	2.539698	1.696103
C	-.380212	3.656213	-.035501
H	.346186	3.156109	-.679258
H	.095657	4.562321	.352481
C	-1.550428	4.045857	-.817891

Table S10. Computed Cartesian coordinates (in Å) of $[Cu^{I}(CYMB)_2]^-$ complex at B3LYP/BS4 level of theory.

Atom	**x**	**y**	**z**
Cu	0.000137	-0.000277	0.000092
O	1.863194	1.330153	0.444478
N	1.286791	-1.384517	-0.645079
N	2.047242	-4.768258	1.359671
C	4.905026	-0.542573	-0.557925
H	5.181815	-1.509586	-0.981821
C	5.903026	0.375662	-0.237173
H	6.951841	0.142321	-0.404451
C	5.517297	1.628851	0.319888
H	6.282847	2.360947	0.578748
C	4.177344	1.929551	0.538621
H	3.878322	2.885110	0.965628
C	3.110987	1.001310	0.222658
C	3.517347	-0.276805	-0.346876
C	2.601582	-1.326040	-0.735059
H	3.106582	-2.202112	-1.173291
C	0.649777	-2.627694	-1.141909
H	1.342705	-3.210006	-1.773665
H	-0.233056	-2.346631	-1.720152
C	0.127646	-3.514797	0.021338
H	-0.468745	-2.875110	0.680349
H	-0.553356	-4.273906	-0.386820
C	1.193702	-4.200268	0.770958
O	-1.863001	-1.330076	-0.446050
N	-1.286537	1.383476	0.646260
N	-2.048200	4.769605	-1.354061
C	-4.904942	0.542563	0.556165
H	-5.181722	1.509220	0.980874
C	-5.903001	-0.375042	0.233803
H	-6.951856	-0.141568	0.400645
C	-5.517282	-1.627743	-0.324367
H	-6.282884	-2.359326	-0.584521
C	-4.177279	-1.928610	-0.542558
H	-3.878261	-2.883789	-0.970413
C	-3.110849	-1.001049	-0.224844
C	-3.517205	0.276607	0.345729
C	-2.601395	1.325224	0.735461
H	-3.106431	2.201014	1.174218
C	-0.649576	2.626160	1.144413
H	-1.342412	3.207569	1.777100
H	0.233470	2.344558	1.722060
C	-0.127966	3.514819	-0.017893
H	0.468391	2.876067	-0.677837
H	0.552999	4.273554	0.391028
C	-1.194378	4.201030	-0.766319

Table S11. Computed Cartesian coordinates (in Å) of $[Cu^{I}(CYMB)_2]^-$ complex at B3LYP/BS5 level of theory. Structure partially optimized.

Atom	x	y	z
Cu	0.000075	-0.000244	-0.000076
O	1.853346	1.288742	0.454829
N	1.307566	-1.410654	-0.646507
N	1.986655	-4.703953	1.416868
C	4.873299	-0.523544	-0.557353
H	5.159592	-1.481262	-0.987444
C	5.853286	0.394711	-0.236987
H	6.900943	0.173861	-0.408589
C	5.455234	1.628512	0.324314
H	6.210187	2.366303	0.586046
C	4.126295	1.912500	0.547327
H	3.822408	2.860245	0.981031
C	3.069461	0.983589	0.232440
C	3.494198	-0.279930	-0.343171
C	2.600694	-1.334594	-0.736738
H	3.117423	-2.196274	-1.183353
C	0.698711	-2.636923	-1.152248
H	1.413139	-3.219634	-1.751817
H	-0.158705	-2.367176	-1.770895
C	0.136285	-3.519755	-0.017556
H	-0.512612	-2.901331	0.608047
H	-0.492437	-4.304794	-0.451505
C	1.169099	-4.165570	0.794206
O	-1.853269	-1.288903	-0.455844
N	-1.307419	1.409921	0.646863
N	-1.987188	4.706960	-1.412388
C	-4.873238	0.523275	0.556483
H	-5.159510	1.480803	0.987008
C	-5.853267	-0.394679	0.235384
H	-6.900937	-0.173781	0.406845
C	-5.455242	-1.628228	-0.326492
H	-6.210231	-2.365772	-0.588815
C	-4.126287	-1.912275	-0.549330
H	-3.822415	-2.859821	-0.983480
C	-3.069405	-0.983685	-0.233654
C	-3.494117	0.279591	0.342509
C	-2.600576	1.333956	0.736795
H	-3.117305	2.195487	1.183697
C	-0.698564	2.635969	1.153162
H	-1.412967	3.218297	1.753130
H	0.158950	2.365982	1.771558
C	-0.136438	3.519442	0.018802
H	0.511151	2.901029	-0.608158
H	0.493592	4.303362	0.452865
C	-1.169485	4.167126	-0.791175

Table S12. Computed Cartesian coordinates (in Å) of [$Cu^{II}(TIMB)_2$] complex at B3LYP/BS4 level of theory.

Atom	**x**	**y**	**z**
Cu	0.000000	0.000001	0.597658
H	3.213679	5.365878	1.765574
H	3.306725	2.881869	1.579317
C	2.318683	4.808725	1.497542
C	2.383091	3.421729	1.393942
H	1.069987	6.592473	1.338770
C	1.102221	5.510371	1.256805
C	6.304137	-1.359500	1.179607
H	3.713281	-1.988103	1.566288
C	1.227474	2.656037	1.047013
C	5.139001	-0.893596	0.355342
O	1.337420	1.332156	0.961664
C	-0.034024	4.789864	0.915014
C	3.852569	-1.355575	0.694085
H	6.328478	0.330996	-0.976016
C	-0.007604	3.361730	0.803480
C	5.336340	-0.031545	-0.729757
H	-0.972220	5.309748	0.725242
C	2.741529	-0.953877	-0.067446
H	-1.069987	-6.592470	1.338776
H	0.972220	-5.309746	0.725248
N	1.416980	-1.399117	0.254502
H	2.077290	-3.361345	0.262885
C	-1.102221	-5.510369	1.256809
C	1.221565	-2.700021	0.434771
C	0.034024	-4.789862	0.915019
H	-3.213680	-5.365876	1.765576
C	-2.318684	-4.808723	1.497544
C	4.213261	0.372505	-1.477229
C	0.007604	-3.361728	0.803484
C	-2.383092	-3.421727	1.393943
H	-3.306726	-2.881867	1.579317
C	-1.227474	-2.656035	1.047015
C	-1.221565	2.700023	0.434767
O	-1.337420	-1.332154	0.961665
C	2.927831	-0.077066	-1.155227
C	4.417100	1.270851	-2.663188
H	-2.077289	3.361347	0.262879
N	-1.416980	1.399118	0.254500
H	2.070232	0.251124	-1.731919
H	-3.713283	1.988110	1.566281
C	-2.741529	0.953879	-0.067448
C	-3.852570	1.355580	0.694079
H	-2.070231	-0.251129	-1.731917
C	-2.927830	0.077063	-1.155227
C	-5.139001	0.893600	0.355337

C	-6.304138	1.359506	1.179600
C	-4.213259	-0.372509	-1.477228
C	-5.336339	0.031544	-0.729759
H	-6.328477	-0.330997	-0.976018
C	-4.417098	-1.270861	-2.663183
F	-5.382005	-2.261681	-2.424055
F	-4.868267	-0.566759	-3.800675
F	-3.246039	-1.929026	-3.056049
F	-6.574138	2.732670	0.993895
F	-7.490029	0.681887	0.885133
F	-6.079674	1.206551	2.559578
F	4.868255	0.566742	-3.800680
F	3.246043	1.929024	-3.056049
F	5.382016	2.261664	-2.424070
F	6.574141	-2.732663	0.993903
F	7.490027	-0.681879	0.885142
F	6.079670	-1.206545	2.559585

Table S13. Computed Cartesian coordinates (in Å) of [$Cu^{II}(TIMB)_2$] complex at B3LYP/BS5 level of theory. Structure partially optimized.

Atom	**x**	**y**	**z**
Cu	0.000000	0.000000	0.504017
H	3.134347	5.402022	1.430474
H	3.263481	2.936913	1.291150
C	2.238444	4.827964	1.215519
C	2.322957	3.453597	1.138098
H	0.963050	6.581396	1.081794
C	1.012690	5.500915	1.020175
C	6.262990	-1.263404	1.424728
H	3.666074	-1.878498	1.683056
C	1.176607	2.658378	0.862794
C	5.147070	-0.842573	0.508057
O	1.310427	1.367934	0.803842
C	-0.113352	4.759432	0.748074
C	3.853609	-1.287543	0.793776
H	6.402038	0.306262	-0.811518
C	-0.069273	3.341495	0.664297
C	5.400446	-0.045364	-0.600813
H	-1.066630	5.256682	0.592314
C	2.796991	-0.939593	-0.045966
H	-0.963049	-6.581395	1.081805
H	1.066631	-5.256682	0.592324
N	1.473237	-1.380937	0.214543
H	2.154890	-3.313432	0.226408
C	-1.012690	-5.500914	1.020184
C	1.285219	-2.665482	0.364937
C	0.113353	-4.759432	0.748082
H	-3.134347	-5.402020	1.430480
C	-2.238444	-4.827963	1.215526
C	4.330230	0.313197	-1.425585
C	0.069273	-3.341494	0.664302
C	-2.322958	-3.453596	1.138101
H	-3.263481	-2.936912	1.291152
C	-1.176607	-2.658377	0.862797
C	-1.285219	2.665482	0.364932
O	-1.310427	-1.367933	0.803843
C	3.039799	-0.121824	-1.155149
C	4.603878	1.135951	-2.655467
H	-2.154889	3.313433	0.226401
N	-1.473237	1.380937	0.214540
H	2.216763	0.169763	-1.794685
H	-3.666075	1.878501	1.683050
C	-2.796991	0.939593	-0.045969
C	-3.853610	1.287545	0.793772
H	-2.216763	-0.169766	-1.794685
C	-3.039798	0.121822	-1.155150
C	-5.147071	0.842575	0.508053

C	-6.262990	1.263408	1.424723
C	-4.330230	-0.313199	-1.425586
C	-5.400446	0.045363	-0.600816
H	-6.402038	-0.306263	-0.811521
C	-4.603877	-1.135956	-2.655466
F	-5.544662	-2.094841	-2.430939
F	-5.074145	-0.369131	-3.683451
F	-3.491479	-1.766256	-3.118431
F	-6.508157	2.605060	1.338645
F	-7.433135	0.631264	1.151724
F	-5.968265	1.014879	2.733038
F	5.074141	0.369123	-3.683451
F	3.491480	1.766254	-3.118430
F	5.544666	2.094833	-2.430942
F	6.508159	-2.605056	1.338651
F	7.433134	-0.631259	1.151730
F	5.968262	-1.014875	2.733043

Table S14. Computed Cartesian coordinates (in Å) of $[Cu^{I}(CTIMB)_2]^-$ complex at B3LYP/BS4 level of theory.

Atom	x	y	z
Cu	0.000000	0.000001	-1.155483
H	-2.382606	5.726229	-3.069983
H	-2.681922	3.251161	-3.115134
C	-1.656559	5.079062	-2.578794
C	-1.832606	3.704908	-2.610275
H	-0.409129	6.742533	-1.886837
C	-0.536076	5.663182	-1.907800
C	-6.328012	-1.418918	0.216229
H	-3.955130	-2.223858	-0.789906
C	-0.902721	2.792458	-1.975278
C	-4.990260	-0.787719	0.448628
O	-1.127433	1.508914	-2.027449
C	0.378370	4.826185	-1.286434
C	-3.847041	-1.374592	-0.123063
H	-5.789314	0.809309	1.682108
C	0.245029	3.395879	-1.294947
C	-4.900855	0.351999	1.260666
H	1.238269	5.255361	-0.769669
C	-2.563799	-0.820718	0.113456
H	0.409131	-6.742530	-1.886847
H	-1.238267	-5.255360	-0.769678
N	-1.383283	-1.343466	-0.457101
H	-2.052522	-3.293558	-0.174520
C	0.536078	-5.663178	-1.907809
C	-1.273099	-2.660722	-0.623677
C	-0.378368	-4.826183	-1.286442
H	2.382608	-5.726223	-3.069991
C	1.656561	-5.079057	-2.578801
C	-3.623610	0.909919	1.477166
C	-0.245028	-3.395877	-1.294953
C	1.832608	-3.704904	-2.610280
H	2.681924	-3.251155	-3.115138
C	0.902722	-2.792455	-1.975282
C	1.273100	2.660723	-0.623672
O	1.127433	-1.508910	-2.027451
C	-2.475244	0.348323	0.911538
C	-3.518693	2.111764	2.365057
H	2.052523	3.293558	-0.174514
N	1.383283	1.343466	-0.457098
H	-1.500280	0.801427	1.056427
H	3.955130	2.223859	-0.789901
C	2.563799	0.820717	0.113459
C	3.847041	1.374592	-0.123059
H	1.500279	-0.801428	1.056428
C	2.475244	-0.348325	0.911539
C	4.990260	0.787717	0.448632

C	6.328012	1.418917	0.216234
C	3.623609	-0.909921	1.477168
C	4.900854	-0.352001	1.260668
H	5.789313	-0.809312	1.682110
C	3.518691	-2.111767	2.365057
F	4.492502	-3.089933	2.076973
F	3.723326	-1.793696	3.733923
F	2.279217	-2.751565	2.306829
F	6.630449	2.435594	1.158966
F	7.394465	0.508259	0.305057
F	6.439354	2.040035	-1.038794
F	-3.723328	1.793691	3.733923
F	-2.279218	2.751562	2.306830
F	-4.492504	3.089930	2.076974
F	-6.630450	-2.435596	1.158961
F	-7.394465	-0.508261	0.305052
F	-6.439354	-2.040036	-1.038799

Table S15. Input coordinates for single point calculations for [$Cu^{II}(CYMB)_2$] (**1**, X-ray data from this work).

Atom	**x**	**y**	**z**
Cu	0.00023697	-0.00000000	-0.00000000
O	0.45023697	-1.46700000	-1.10800000
N	-1.94976303	-0.18400000	-0.44100000
N	-4.41276303	-1.90100000	1.86400000
C	-2.43276303	-2.89000000	-2.86600000
H	-3.34676303	-2.75200000	-2.97200000
C	-1.82976303	-3.91400000	-3.53200000
H	-2.32776303	-4.48000000	-4.07800000
C	-0.46476303	-4.10200000	-3.38500000
H	-0.04876303	-4.79600000	-3.84300000
C	0.29023697	-3.28000000	-2.57100000
H	1.20523697	-3.42800000	-2.49100000
C	-0.30676303	-2.22400000	-1.86100000
C	-1.69076303	-2.02500000	-2.01100000
C	-2.41676303	-1.01400000	-1.30400000
H	-3.32576303	-0.95000000	-1.49000000
C	-2.93776303	0.73300000	0.14800000
H	-3.76176303	0.68700000	-0.36300000
H	-2.60376303	1.64200000	0.09300000
C	-3.23076303	0.39300000	1.60400000
H	-2.39876303	0.38900000	2.10200000
H	-3.79976303	1.08200000	1.98200000
C	-3.88676303	-0.90800000	1.75700000
O	-0.44976303	1.46700000	1.10800000
N	1.94923697	0.18400000	0.44100000
N	4.41223697	1.90100000	-1.86400000
C	2.43323697	2.89000000	2.86600000
H	3.34623697	2.75200000	2.97200000
C	1.83023697	3.91400000	3.53200000
H	2.32723697	4.48000000	4.07800000
C	0.46523697	4.10200000	3.38500000
H	0.04823697	4.79600000	3.84300000
C	-0.29076303	3.28000000	2.57100000
H	-1.20476303	3.42800000	2.49100000
C	0.30623697	2.22400000	1.86100000
C	1.69023697	2.02500000	2.01100000
C	2.41723697	1.01400000	1.30400000
H	3.32623697	0.95000000	1.49000000
C	2.93823697	-0.73300000	-0.14800000
H	3.76123697	-0.68700000	0.36300000
H	2.60323697	-1.64200000	-0.09300000
C	3.23023697	-0.39300000	-1.60400000
H	2.39823697	-0.38900000	-2.10200000
H	3.80023697	-1.08200000	-1.98200000
C	3.88623697	0.90800000	-1.75700000

Table S16. Input coordinates for single point calculations for [$Cu^{II}(TIMB)_2$] (**2**, X-ray data from [$Cu^{II}(DIMB)_2$] (Corsini 2003); coordinates for CF_3 group atoms in the place of CH_3 were generated via GaussView graphic package.

Atom	**x**	**y**	**z**
Cu	0.00041199	0.53401498	-0.00043820
H	-5.65258801	2.81501498	-0.23443820
H	-3.72158801	2.44501498	-1.35743820
C	-4.97458801	2.32801498	0.17356180
C	-3.81658801	2.10301498	-0.49743820
H	-5.96458801	1.97701498	1.92856180
C	-5.16458801	1.83501498	1.47556180
C	-1.10858801	-0.54898502	-6.34243820
H	0.32041199	0.41701498	-4.31543820
C	-2.74858801	1.36801498	0.06556180
C	-1.10458801	-0.88698502	-4.89143820
O	-1.67458801	1.15901498	-0.64043820
C	-4.14058801	1.13901498	2.05856180
C	-0.23858801	-0.26098502	-4.01043820
H	-2.59958801	-2.24098502	-4.94843820
C	-2.91958801	0.90201498	1.39856180
C	-1.97358801	-1.85398502	-4.38043820
H	-4.25458801	0.81101498	2.92156180
C	-0.19658801	-0.63798502	-2.67443820
H	5.96441199	1.97701498	-1.92843820
H	4.25441199	0.81101498	-2.92143820
N	0.69041199	0.00701498	-1.75943820
H	2.13541199	-0.07598502	-2.98043820
C	5.16441199	1.83501498	-1.47543820
C	1.90041199	0.23201498	-2.13543820
C	4.14041199	1.13901498	-2.05843820
H	5.65241199	2.81501498	0.23456180
C	4.97441199	2.32801498	-0.17343820
C	-1.93558801	-2.25598502	-3.05843820
C	2.91941199	0.90201498	-1.39843820
C	3.81641199	2.10301498	0.49756180
H	3.72141199	2.44501498	1.35756180
C	2.74841199	1.36801498	-0.06543820
C	-1.90058801	0.23201498	2.13556180
O	1.67441199	1.15901498	0.64056180
C	-1.03658801	-1.63998502	-2.20143820
C	-2.84158801	-3.34698502	-2.56843820
H	-2.13558801	-0.07598502	2.98056180
N	-0.68958801	0.00701498	1.75956180
H	-0.99458801	-1.89598502	-1.30943820
H	-0.31958801	0.41701498	4.31556180
C	0.19641199	-0.63798502	2.67456180
C	0.23841199	-0.26098502	4.01056180
H	0.99441199	-1.89598502	1.30856180
C	1.03641199	-1.63998502	2.20156180

C	1.10441199	-0.88698502	4.89156180
C	1.10841199	-0.54898502	6.34256180
C	1.93541199	-2.25598502	3.05856180
C	1.97341199	-1.85398502	4.38056180
H	2.59941199	-2.24098502	4.94856180
C	2.84141199	-3.34698502	2.56856180
F	2.36398474	-0.66134052	6.82569046
F	0.67510499	0.71857862	6.50997586
F	0.29337478	-1.39780615	7.00416367
F	3.70172712	-3.69279796	3.54977089
F	2.10321924	-4.42123122	2.21704144
F	3.53593974	-2.90833591	1.49724571
F	-0.29355081	-1.39780615	-7.00404008
F	-0.67528102	0.71857862	-6.50985227
F	-2.36369289	-0.66129865	-6.82679076
F	-2.10339527	-4.42123122	-2.21691785
F	-3.53508112	-2.90810094	-1.49654825
F	-3.70190315	-3.69279796	-3.54964729

Table S17. Total electronic energy (Eel, Hartrees) for calculated free-ligands and complexes, at different levels of theory (see text for details).

Structure	Level of Theory	Charge/Multiplicity	Eel
Cu^{2+}	BS1	2/2	-195.064882226
Cu^{+}	BS1	1/1	-195.829202120
$CYMB^{-}$	BS1	-1/1	-571.120559200
	BS2	-1/1	-571.227443014
	BS3	-1/1	-571.388863342
$[Cu^{II}(CYMB)_2]$, (**1**)	BS4	0/2	-1338.43824956
	BS5	0/2	-1338.88444290
	BS6	0/2	-1338.93434447
	SP-BS4	0/2	-1338.08399415
	SP-BS5	0/2	-1338.56346530
	SP-BS6	0/2	-1338.62364460
$[Cu^{I}(CYMB)_2]^{-}$	BS4	-1/1	-1338.50450339
	BS5	-1/1	-1338.96396418*
$TIMB^{-}$	BS1	-1/1	-1305.43420984
	BS2	-1/1	-1305.80466534
	BS3	-1/1	-1305.84412691
$[Cu^{II}(TIMB)_2]$, (**2**)	BS4	0/2	-2806.99824039
	BS5	0/2	-2807.70998540*
	SP-BS4	0/2	-2806.57931451
	SP-BS5	0/2	-2807.34124164
$[Cu^{I}(TIMB)_2]^{-}$	BS4	-1/1	-2807.09197595

*Structure partially optimized.

Table S18. Selected geometrical parameters (bond distances, bond angles and torsion angles) for the fully optimized structures $CYMB^-$ free-ligand and $[Cu^{II}(CYMB)_2]$ and $[Cu^{I}(CYMB)_2]^-$ complexes, at different levels of theory (see text for details). X-ray data for the copper(II) complex (**1**, from this work) have been included for comparative purposes.

Vector	**Free-ligand, $CYMB^-$**			**Complex, $[Cu^{II}(CYMB)_2]$**				**Complex, $[Cu^{I}(CYMB)_2]^-$**	
	BS1	**BS2**	**BS3**	**BS4**	**BS5**	**BS6**	**X-Ray, (1)**	**BS4**	**BS5***
Cu1-O1				1.939	1.933	1.941	1.893(3)	2.332	2.303
Cu1-N1				2.030	2.044	2.045	2.007(3)	1.997	2.029
O1-C5	1.290	1.251	1.250	1.338	1.304	1.304	1.308(5)	1.309	1.273
N1-C7	1.313	1.294	1.288	1.318	1.298	1.296	1.285(5)	1.319	1.298
N1-C8	1.464	1.436	1.436	1.484	1.464	1.466	1.472(5)	1.483	1.459
N2-C10	1.182	1.162	1.154	1.181	1.159	1.153	1.129(5)	1.182	1.160
C1-C2	1.396	1.383	1.382	1.392	1.379	1.377	1.363(6)	1.394	1.381
C1-C6	1.428	1.415	1.413	1.427	1.416	1.416	1.425(6)	1.429	1.417
C2-C3	1.428	1.417	1.415	1.421	1.408	1.407	1.386(6)	1.425	1.413
C3-C4	1.388	1.374	1.373	1.395	1.382	1.380	1.381(6)	1.391	1.377
C4-C5	1.467	1.462	1.458	1.427	1.420	1.420	1.406(6)	1.449	1.442
C5-C6	1.477	1.474	1.472	1.436	1.428	1.428	1.406(6)	1.457	1.452
C6-C7	1.451	1.440	1.442	1.439	1.431	1.431	1.431(5)	1.446	1.437
C8-C9	1.561	1.552	1.550	1.553	1.543	1.543	1.523(6)	1.553	1.544
C9-C10	1.472	1.465	1.461	1.472	1.464	1.461	1.466(6)	1.472	1.464
O1-Cu1-N1				90.84	90.89	90.80	91.8(1)	86.69	86.18
N1-Cu1-O1’				89.16	89.11	89.21	88.2(1)	93.31	93.82
O1-Cu1-O1’				179.99	179.99	179.98	180	179.95	179.98
N1-Cu1-N1’				179.99	179.99	179.98	180	179.97	179.98
Cu1-O1-C5				130.97	130.76	130.64	130.3(3)	125.86	126.87
Cu1-N1-C7				124.66	123.87	123.90	124.1(3)	129.31	128.55
Cu1-N1-C8				118.62	119.43	119.49	120.5(4)	114.37	115.19
C2-C1-C6	123.40	123.36	123.43	121.43	121.64	121.66	121.3(4)	122.62	122.79
C1-C2-C3	117.99	117.94	117.90	118.88	118.65	118.65	119.1(4)	118.41	118.23
C2-C3-C4	120.91	121.24	121.22	121.00	121.20	121.21	121.4(4)	120.84	121.09
C3-C4-C5	123.42	123.47	123.42	121.03	121.34	121.38	120.8(4)	122.44	122.62

O1-C5-C4	120.32	121.19	121.12	118.95	118.97	118.97	118.6(4)	120.24	120.50
O1-C5-C6	125.05	124.82	124.70	122.99	123.65	123.68	123.3(4)	123.52	123.86
C4-C5-C6	114.63	113.98	114.18	118.05	117.38	117.35	118.0(4)	116.23	115.64
C1-C6-C5	119.64	120.00	119.84	119.61	119.79	119.75	119.4(4)	119.46	119.62
C1-C6-C7	115.55	116.21	115.91	118.04	117.56	117.58	117.4(4)	116.14	115.95
C5-C6-C7	124.80	123.78	124.24	122.36	122.65	122.66	123.1(4)	124.39	124.42
N1-C7-C6	129.06	128.52	129.02	128.05	128.13	128.24	127.1(4)	130.18	130.02
N1-C8-C9	110.03	110.83	111.07	111.91	112.15	112.14	111.9(4)	111.86	112.19
C7-N1-C8	117.49	116.62	117.10	116.72	116.69	116.60	115.3(4)	116.26	116.14
C8-C9-C10	113.67	114.17	114.28	112.84	112.64	112.77	112.6(4)	113.81	113.75
N2-C10-C9	178.23	177.42	177.40	178.88	178.38	178.33	178.7(5)	178.93	178.34
Cu1-N1-C8-C9				79.4	78.1	78.4	76.1(2)	75.2	73.9
N1-C8-C9-C10	83.4	78.3	80.0	66.5	65.9	64.1	65.6(2)	73.5	71.6
C8-C9-C10-N2	98.1	114.1	110.4	3.6	12.9	15.3	70.9(2)	93.2	90.9

*Structure partially optimized.

Table S19. Selected geometrical parameters (bond distances and bond angles) for the fully optimized structures $TIMB^-$ free-ligand and $[Cu^{II}(TIMB)_2]$ and $[Cu^{I}(TIMB)_2]^-$ complexes, at different levels of theory (see text for details). X-ray data for the copper(II) complex analogous $[Cu^{II}(DIMB)_2]$ (Corsini 2003) have been included for comparative purposes.

Vector	**Free-ligand, $TIMB^-$**			**Complex, $[Cu^{II}(TIMB)_2]$**			**Complex, $[Cu^{I}(TIMB)_2]^-$**
	BS1	**BS2**	**BS3**	**BS4**	**BS5***	**X-Ray $[Cu^{II}(TIMB)_2]$**	**BS4**
Cu1-O1				1.922	1.918	1.898	2.076
Cu1-N1				2.021	2.040	1.962	2.051
O1-C5	1.283	1.247	1.245	1.331	1.299	1.302	1.304
N1-C7	1.327	1.307	1.304	1.328	1.307	1.287	1.332
N1-C8	1.381	1.368	1.369	1.434	1.419	1.428	1.411
C1-C2	1.387	1.376	1.375	1.388	1.375	1.368	1.387
C1-C6	1.437	1.423	1.422	1.433	1.421	1.408	1.436
C2-C3	1.435	1.423	1.422	1.425	1.412	1.405	1.431
C3-C4	1.382	1.370	1.368	1.392	1.379	1.357	1.386
C4-C5	1.470	1.463	1.462	1.429	1.422	1.413	1.449
C5-C6	1.482	1.477	1.476	1.443	1.435	1.422	1.464
C6-C7	1.429	1.422	1.422	1.431	1.423	1.425	1.431
C8-C9	1.428	1.417	1.416	1.409	1.399	1.390	1.418
C8-C13	1.431	1.417	1.415	1.406	1.394	1.389	1.417
C9-C10	1.398	1.387	1.386	1.399	1.388	1.386	1.398
C10-C11	1.412	1.401	1.401	1.408	1.398	1.382	1.410
C11-C12	1.405	1.394	1.392	1.400	1.389	1.397	1.402
C12-C13	1.405	1.394	1.394	1.408	1.398	1.385	1.406
C10-C14	1.496	1.499	1.496	1.502	1.505	1.500	1.498
C12-C15	1.497	1.499	1.497	1.501	1.504	1.490	1.497
C14-F14(av)	1.421	1.374	1.366	1.412	1.362		1.420
	1.411	1.370	1.373	1.404	1.366		1.410
	1.402	1.362	1.378	1.400	1.360		1.396
C15-F15(av)	1.409	1.368	1.377	1.397	1.358		1.405
	1.420	1.373	1.370	1.412	1.364		1.419
	1.406	1.365	1.370	1.406	1.367		1.405

O1-Cu1-N1				92.30	91.88	94.6	91.90
N1-Cu1-O1’				91.38	90.66	95.5	104.65
N1-Cu1-N1’				160.44	163.68	148.8	140.18
O1-Cu1-O1’				158.17	162.01	141.6	130.32
Cu1-O1-C5				130.08	130.20	126.7	127.24
Cu1-N1-C7				123.51	123.03	127.1	123.32
Cu1-N1-C8				118.09	119.28	118.5	117.33
N1-C7-C6	128.28	128.15	128.39	127.80	127.88	118.5	128.75
N1-C8-C9	117.98	118.16	118.32	119.24	119.27	118.9	118.72
N1-C8-C13	124.81	124.69	124.55	121.31	121.25	120.8	123.02
C7-N1-C8	121.55	119.98	119.75	118.07	117.44	118.4	128.75
C2-C1-C6	123.03	123.12	123.14	121.43	121.61	122.3	122.49
C1-C2-C3	118.49	118.34	118.31	119.00	118.76	118.2	118.70
C2-C3-C4	121.02	121.33	121.34	121.16	121.36	121.0	121.00
C3-C4-C5	123.06	123.07	123.14	120.96	121.25	122.3	122.20
O1-C5-C4	120.28	121.03	121.10	118.79	118.77	119.4	119.44
O1-C5-C6	124.72	124.47	124.47	123.10	123.80	123.7	124.00
C4-C5-C6	114.99	114.50	114.43	118.10	117.42	116.9	116.55
C1-C6-C5	119.39	119.62	119.63	119.34	119.59	119.2	119.06
C1-C6-C7	116.16	116.35	116.23	117.73	117.38	117.2	116.23
C5-C6-C7	124.46	124.02	124.14	122.92	123.02	123.6	124.70
C9-C8-C13	117.10	117.04	117.03	119.43	119.47	120.3	118.20
C8-C9-C10	121.04	121.09	121.11	119.92	119.92	120.1	120.50
C9-C10-C11	121.72	121.59	121.56	121.21	121.08	118.7	121.52
C10-C11-C12	117.56	117.71	117.72	118.40	118.59	122.3	117.91
C11-C12-C13	121.92	121.73	121.70	121.15	120.99	118.0	121.51
C12-C13-C8	120.63	120.81	120.84	119.87	119.94	120.5	120.33
C9-C10-C14	119.82	119.86	119.84	119.91	119.97	120.8	120.31
C13-C12-C15	119.22	119.14	118.79	118.36	118.23	121.2	119.16
C10-C14-F14	113.19	112.47	112.51	112.42	111.76		112.43
	113.03	112.66	112.79	112.40	112.07		112.78
	113.90	113.40	113.56	112.92	112.52		113.90
C12-C15-F15	113.37	112.96	113.24	113.11	112.74		113.27

	113.24	112.52	112.52	112.21	111.92	112.91
	113.59	113.10	113.12	112.40	111.68	113.32
F-C14-F	105.17	112.47	105.74	105.64	107.15	105.71
	106.15	112.47	105.26	106.92	106.60	106.66
	104.57	113.40	106.31	106.01	106.35	104.64
F-C15-F	106.11	106.39	105.57	106.83	106.85	106.43
	104.79	105.67	106.24	106.36	107.11	105.10
	104.91	105.57	105.48	105.39	107.11	105.06

*Structure partially optimized.

Table S20. Mulliken atomic charges (e) for fully optimized structures $CYMB^-$ and $TIMB^-$ free-ligands, and $[Cu^{I/II}(CYMB)_2]^{-/0}$ and $[Cu^{I/II}(TIMB)_2]^{-/0}$ complexes, at different levels of theory (see text for details). Values from single point (SP) calculation for copper(II) complexes from X-ray structures have been included for comparative purposes.

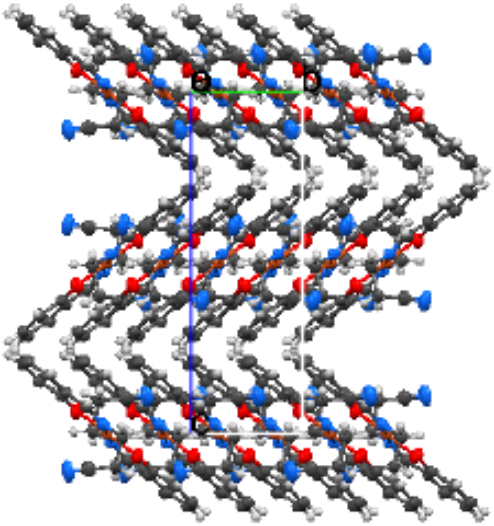
Atom	**Free-ligand, $CYMB^-$**			**Complex, $[Cu^{II}(CYMB)_2]$ (1)**						**Complex, $[Cu^{I}(CYMB)_2]^-$**
	BS1	**BS2**	**BS3**	**BS4**	**BS5**	**BS6**	**SP-BS4**	**SP-BS5**	**SP-BS6**	**BS4**
Cu1				0.64508	0.92203	-1.01224	0.676471	0.97401	-1.07254	0.27122
O1	-0.38078	-0.61612	-0.39713	-0.53628	-0.76957	0.12047	-0.53132	-0.78843	0.12853	-0.43886
N1	-0.03997	-0.41030	0.07909	-0.27071	-0.73794	0.37177	-0.25938	-0.72207	0.20370	-0.21546
N2	-0.06570	-0.49993	-0.34133	-0.03364	-0.31349	-0.54135	0.00924	-0.31610	-0.55875	-0.06747
C1	-0.35331	-0.12991	-0.89800	-0.32268	-0.20497	-0.20463	-0.40169	-0.17692	-0.16411	-0.34246
H1	0.17267	0.02473	0.09881	0.21910	0.14950	0.17287	0.31442	0.07429	0.22998	0.19271
C2	-0.32278	-0.13871	-0.39591	-0.26601	-0.16317	-0.18641	-0.33934	-0.10619	-0.36796	-0.30216
H2	0.18120	0.01102	0.09659	0.22649	0.15144	0.16533	0.31188	0.09219	0.24515	0.19715
C3	-0.19804	-0.08034	-0.26080	-0.17814	-0.14895	-0.13850	-0.26218	-0.11510	-0.25251	-0.19272
H3	0.17322	0.01740	0.11080	0.22187	0.15647	0.15118	0.30801	0.09820	0.19628	0.19134
C4	-0.36620	-0.15374	0.14056	-0.35339	-0.21697	0.02670	-0.44924	-0.18792	0.00872	-0.36529
H4	0.19869	0.02136	0.12837	0.22371	0.14696	0.17646	0.31660	0.08525	0.25167	0.20769
C5	-0.00252	0.35078	-0.77427	0.27132	0.62772	0.19118	0.26266	0.67684	0.03767	0.14929
C6	0.30119	0.02923	1.13976	0.28892	-0.11712	-0.06444	0.21831	0.00601	-0.05462	0.29813
C7	-0.35086	0.09149	-0.02127	-0.18559	0.27872	-0.28785	-0.26867	0.24041	0.05012	-0.22338
H7	0.13753	0.00977	0.02158	0.22661	0.14786	0.06640	0.31300	0.12935	0.12772	0.17843
C8	-0.35097	-0.01740	-0.16177	-0.29891	-0.14584	-0.37461	-0.34885	-0.23340	-0.50149	-0.29945
H8a	0.13676	0.04979	0.04009	0.19279	0.17121	0.14467	0.23020	0.18204	0.21992	0.14963
H8b	0.18724	0.07582	0.16438	0.25875	0.23065	0.23610	0.28541	0.26460	0.23853	0.26324
C9	-0.36996	-0.24834	-0.04264	-0.38568	-0.36669	-0.17909	-0.44036	-0.39599	-0.36870	-0.38490
H9a	0.26465	0.16400	0.19514	0.29147	0.24491	0.29979	0.32513	0.25462	0.35160	0.30905
H9b	0.18718	0.10800	0.11930	0.23085	0.19981	0.20856	0.26375	0.22093	0.23841	0.21159
C10	-0.13925	0.34140	-0.04136	-0.14338	0.21842	0.15162	-0.19581	0.22963	0.27642	-0.15168

Atom	Free-ligand, $TIMB^-$			Complex, $[Cu^{II}(TIMB)_2]$ (2)				Complex, $[Cu^{I}(TIMB)_2]^-$
	BS1	BS2	BS3	BS4	BS5*	SP-BS4	SP-BS5	BS4
Cu1				0.60704	0.82093	0.54688	0.68814	0.23714
O1	-0.34028	-0.43845	-0.49530	-0.50023	-0.71950	-0.46857	-0.68687	-0.41059
N1	-0.03235	-0.43947	-0.29460	-0.35292	-0.82859	-0.35311	-0.86390	-0.258072
C1	-0.33419	-0.25498	-0.24828	-0.31928	-0.22240	-0.39482	-0.21444	-0.33027
H1	0.18565	0.11214	0.11193	0.21984	0.14974	0.31162	0.07285	0.19615
C2	-0.31163	-0.18576	-0.23287	-0.26641	-0.14896	-0.35191	-0.10178	-0.29621
H2	0.19158	0.11251	0.13873	0.23062	0.15251	0.31428	0.09609	0.20393
C3	-0.19311	-0.17614	-0.36692	-0.17306	-0.13837	-0.25245	-0.10525	-0.18588
H3	0.18513	0.11580	0.11814	0.22856	0.16150	0.31267	0.09975	0.20060
C4	-0.35099	-0.25089	-0.18043	-0.34712	-0.22145	-0.43059	-0.20172	-0.35400
H4	0.21120	0.12837	0.11179	0.24261	0.16327	0.33104	0.10391	0.22802
C5	-0.00835	0.30170	0.73828	0.27432	0.64748	0.24874	0.71054	0.19195
C6	0.32248	-0.03271	-0.34665	0.29654	-0.11700	0.23860	0.00385	0.29593
C7	-0.39811	0.00633	-0.07314	-0.26830	0.20268	-0.32040	0.23575	-0.29707
H7	0.16902	0.07414	0.12341	0.248830	0.17106	0.33288	0.12932	0.20617
C8	0.28346	0.26953	-0.25571	0.50139	0.18907	0.47160	0.45477	0.43906
C9	-0.50801	-0.10291	-0.17857	-0.43018	0.06222	-0.45378	-0.01535	-0.43521
H9	0.28668	0.17392	0.19616	0.27480	0.18546	0.35962	0.10593	0.28857
C10	0.38128	-0.40861	-0.09977	0.37278	-0.43872	0.28958	-0.32465	0.37385
C11	-0.51838	-0.07317	-0.02154	-0.50054	-0.01039	-0.56043	-0.10394	-0.49597
H11	0.27204	0.15571	0.22067	0.29484	0.17872	0.37511	0.08219	0.27699
C12	0.38593	-0.42185	0.08768	0.37878	-0.42330	0.30286	-0.28106	0.38261
C13	-0.49297	-0.14787	-0.23894	-0.44191	-0.04433	-0.55121	-0.15773	-0.48312
H13	0.27054	0.16742	0.22371	0.28008	0.18787	0.37547	0.09079	0.27402
C14	0.28942	0.58154	0.31550	0.28986	0.59914	0.29817	0.60876	0.27727
C15	0.27985	0.58664	0.27301	0.28986	0.59953	0.29988	0.61235	0.27866
F14a	-0.20862	-0.14509	-0.10989	-0.18750	-0.12446	-0.16462	-0.11658	-0.20458
F14b	-0.20767	-0.14713	-0.10555	-0.18735	-0.12588	-0.17103	-0.11104	-0.18481
F14c	-0.19632	-0.13372	-0.09923	-0.18767	-0.12444	-0.16459	-0.11604	-0.19867
F15a	-0.20631	-0.14622	-0.10296	-0.19061	-0.12614	-0.16695	-0.11544	-0.20195
F15b	-0.20631	-0.14457	-0.11102	-0.18570	-0.12491	-0.16396	-0.11971	-0.19908

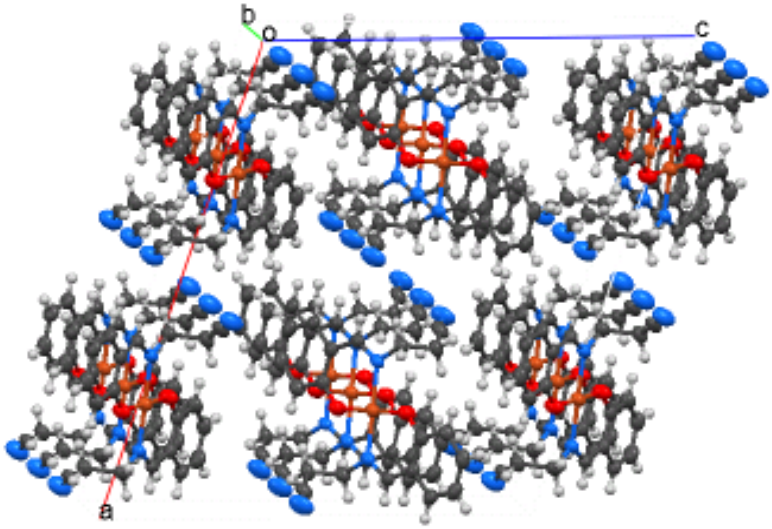
F15c	-0.20066	-0.13622	-0.09763	-0.18825	-0.12183	-0.16714	-0.11540	-0.19686

*Structure partially optimized.

Figure S1. Crystal packing of (**I**) as viewed almost along the (a) **a** cell edge and (b) **b** cell edge.



(a)



(b)