

The trivalent copper complex of a conjugated bis-dithiocarbamate Schiff base: stabilisation of Cu in three different oxidation states.

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Supporting Information

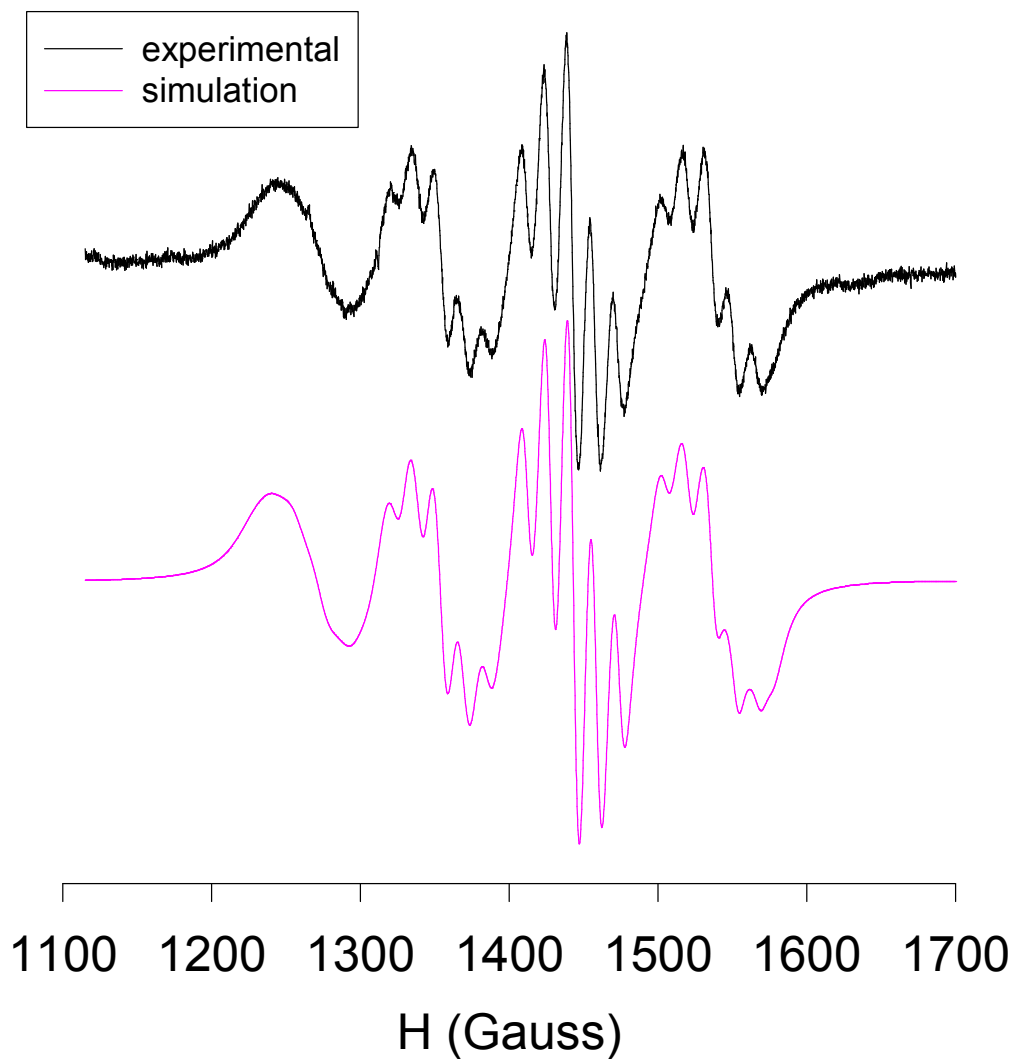


Figure S1. Experimental and simulated room temperature S-band (4.050 GHz) EPR spectra of $[\text{Cu}^{\text{II}}(\text{ttfasbz})]^-$ (1 mM in DMF) generated by reduction of $[\text{Cu}^{\text{III}}\text{L}]$ with cobaltocene. Relevant spin Hamiltonian parameters: g_{iso} 2.0545; A_{iso} 84.10; A_{N} $14.66 \times 10^{-4} \text{ cm}^{-1}$. Note the organic radical signal is absent due to decay over time.

Table S1. The energies of the calculated $[\text{Cu}(\text{tffasbz})]^n$ species relative to the $n=0$ $S=1$ solution. S , UKS, RKS and BS have their usual meanings. Single-point energies are taken from single point B3LYP calculations and the zero-point energies from B3LYP vibrational frequency calculations. (Note, 1 hartree = 627.503 kcal mol⁻¹.)

n	S	method	Geometry	Single-point (hartree)	Zero-point (hartree)
0	1	UKS	X-ray	-5074.56682	n.a.
0	0	RKS	X-ray	-5074.58975	n.a.
0	0	BS(1,1)	X-ray	-5074.58975	n.a.
0	1	UKS	B3LYP	-5074.92693	0.37702
0	0	RKS	B3LYP	-5074.93152	0.37771
0	0	BS(1,1)	B3LYP	-5074.93176	0.37784
1-	0.5	UKS	B3LYP	-5075.04412	0.37694
2-	0	RKS	B3LYP	-5075.00178	0.37203

Figure S2. DFT calculated spin density plots (yellow: positive; red: negative) and Mulliken populations for $[\text{Cu}(\text{tffasbz})]^0$ obtained from $S=1$ UKS (left) and $S=0$ BS(1,1) (right) calculations.

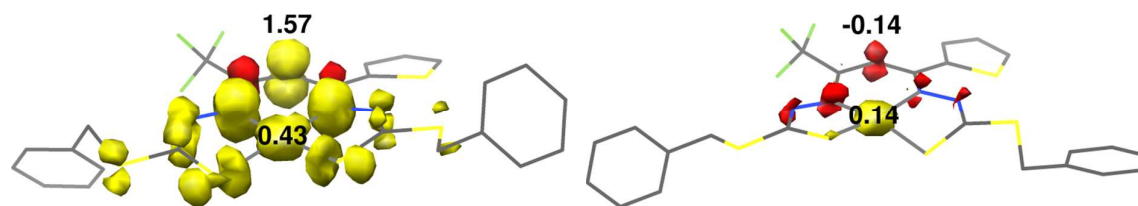
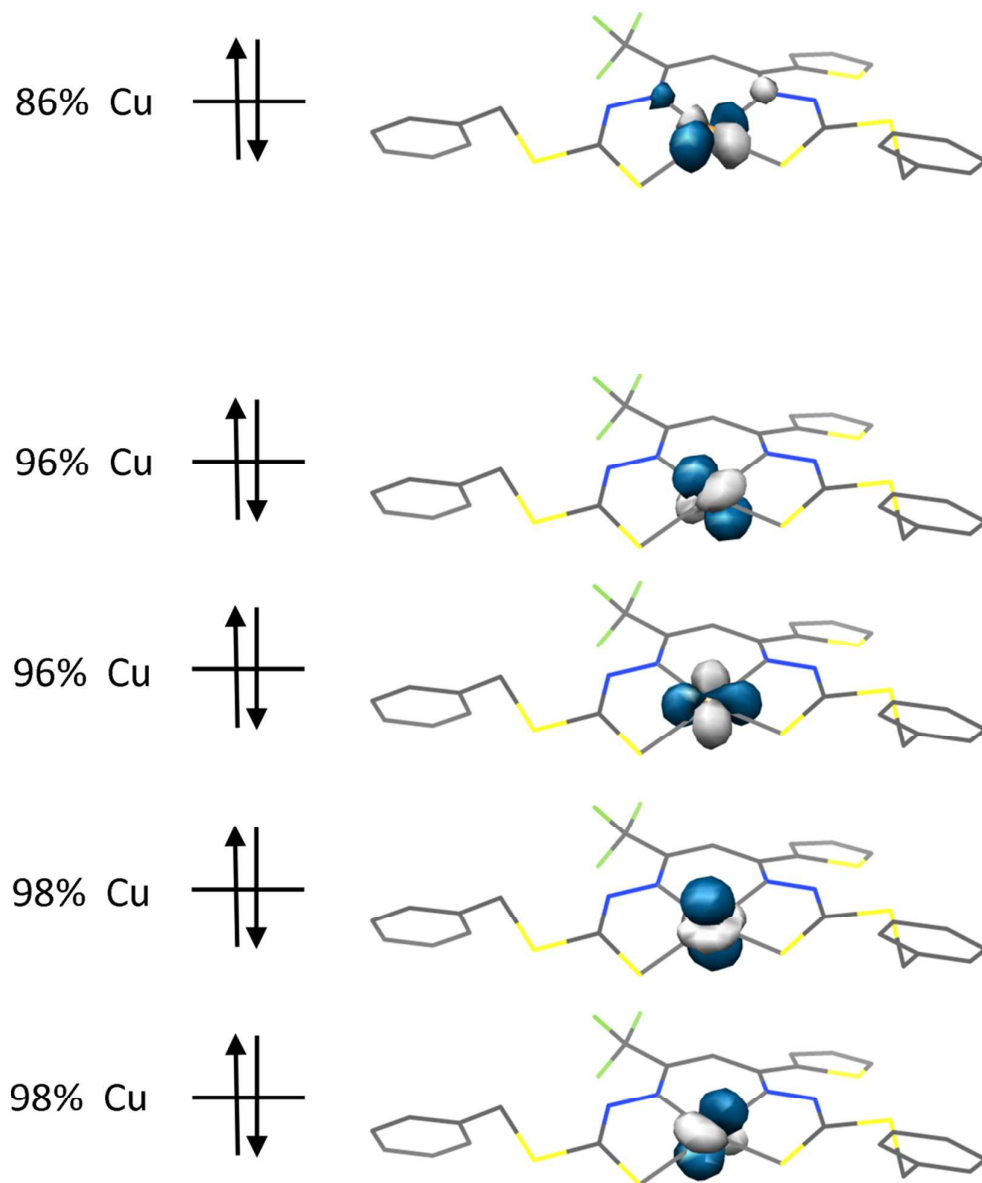


Figure S2. Qualitative frontier molecular orbital diagram for $S = 0$ $[\text{Cu}(\text{ttfasbz})]^{2-}$ calculated via a B3LYP RKS single point calculation using atomic coordinates taken from the corresponding B3LYP geometry optimized structure. The doubly occupied Cu d-orbitals are depicted using localized quasi-restricted orbitals.



DFT geometry optimized atomic xyz coordinates for [Cu(ttfasbz)]ⁿ (n = 0, 1-, 2-).

[Cu(ttfasbz)]⁰, S = 0, RKS

Cu	2.153338	3.667203	4.877113
C	3.681266	3.253497	7.300920
C	3.959512	3.283162	10.067510
H	4.097610	4.358850	9.982913
H	2.892379	3.068125	10.067645
C	1.286428	5.665764	6.752551
C	1.495139	6.478122	8.039352
C	0.390885	6.174757	5.826422
H	-0.181187	7.016866	6.171376
C	0.106759	5.748543	4.508457
C	1.142072	3.407637	2.185636
C	1.587205	1.595631	0.014598
H	2.536997	1.425161	0.515785
H	0.854716	0.875798	0.379711
C	-1.021760	6.389019	3.819842
C	-1.657083	7.556650	4.207573
H	-1.323979	8.176458	5.026540
C	-2.776431	7.888909	3.419301
H	-3.380414	8.771276	3.574138
C	-3.006548	6.963647	2.436438
H	-3.787303	6.971475	1.691284
C	4.639329	2.729158	11.285187
C	5.735034	3.384900	11.849137
H	6.103820	4.295939	11.392082
C	6.348301	2.886442	12.992658
H	7.189530	3.413166	13.425437
C	5.873327	1.722415	13.586888
H	6.346693	1.334643	14.479944
C	4.785166	1.058076	13.029364
H	4.405607	0.154631	13.489761
C	4.174196	1.558658	11.886876
H	3.324445	1.040997	11.457009
C	1.745280	1.529808	-1.481897
C	3.010379	1.625358	-2.063442
H	3.884546	1.719765	-1.429747
C	3.158187	1.606133	-3.445651
H	4.146831	1.678595	-3.882006
C	2.040527	1.501558	-4.266613
H	2.155944	1.495265	-5.343702
C	0.775670	1.400887	-3.697166
H	-0.099089	1.313818	-4.329214
C	0.630831	1.410648	-2.314965
H	-0.357817	1.332929	-1.877973
N	2.829900	4.186081	7.590982
N	1.961400	4.512798	6.608207
N	0.874715	4.808338	3.930100
N	0.520606	4.434910	2.691245
F	2.770660	6.881820	8.168690
F	1.157859	5.789668	9.141825
F	0.740774	7.598811	8.041257
S	3.975339	2.682208	5.681717
S	4.670360	2.515957	8.548341
S	2.074534	2.292092	3.129044
S	0.993826	3.290601	0.437183
S	-1.838734	5.716387	2.434601

[Cu(ttfasbz)]⁰, S = 1, UKS

Cu	2.340591	2.946656	4.891123
C	4.168157	2.541640	7.181394
C	5.550854	3.370184	9.528764
H	6.629305	3.487577	9.634835
H	5.154684	4.247275	9.021831
C	2.025162	5.231376	6.745894
C	2.469158	6.105572	7.926652
C	0.952878	5.682438	5.995394
H	0.535617	6.608863	6.344758
C	0.328687	5.169854	4.818206
C	0.983284	2.915888	2.277092
C	1.569981	1.608778	-0.151174
H	2.553032	1.799479	0.277225
H	1.256123	0.606065	0.134457
C	-0.904028	5.838441	4.391019
C	-1.664552	6.686117	5.182323
H	-1.423204	6.928343	6.206267
C	-2.813623	7.189582	4.543506
H	-3.520713	7.856884	5.015054
C	-2.932838	6.724969	3.261665
H	-3.709338	6.950319	2.547134
C	4.901400	3.167560	10.871786
C	5.670632	3.205872	12.035304
H	6.745056	3.335776	11.963829
C	5.072975	3.100178	13.287878
H	5.684712	3.140431	14.180540
C	3.695701	2.952808	13.390741
H	3.226117	2.877063	14.363637
C	2.921360	2.899124	12.234720
H	1.847146	2.779713	12.306972
C	3.519359	3.000657	10.986836
H	2.910644	2.962569	10.093283
C	1.597080	1.765263	-1.648043
C	2.255070	2.847767	-2.239340
H	2.714378	3.601402	-1.610726
C	2.331297	2.959234	-3.620985
H	2.853362	3.797424	-4.065577
C	1.749264	1.991110	-4.434659
H	1.816842	2.078045	-5.512330
C	1.087647	0.913410	-3.856926
H	0.634182	0.154305	-4.481984
C	1.011941	0.804300	-2.471758
H	0.504978	-0.043059	-2.024774
N	3.586670	3.709400	7.403906
N	2.666349	4.073910	6.517354
N	0.901286	4.165874	4.152483
N	0.427051	3.918188	2.927056
F	3.769549	6.440828	7.844967
F	2.267283	5.508713	9.114499
F	1.780987	7.266818	7.963687
S	3.859219	1.495170	5.855990
S	5.343039	1.974079	8.340348
S	2.137393	1.815135	2.919531
S	0.424704	2.826120	0.614619
S	-1.666313	5.658520	2.833985

[Cu(TTFASBZ)]⁰, S = 0, BS(1,1)

Cu	2.256143	3.691599	4.856717
C	3.763803	3.275801	7.299363
C	3.971317	3.302489	10.069645
H	4.128387	4.376154	9.990854
H	2.901673	3.103953	10.034915
C	1.403865	5.713738	6.717370
C	1.661719	6.561927	7.971787
C	0.500238	6.211025	5.796159
H	-0.023391	7.093305	6.115735
C	0.174465	5.745153	4.498335
C	1.235960	3.435977	2.161558
C	1.645818	1.628610	-0.018138
H	2.614407	1.454047	0.444360
H	0.924009	0.916370	0.381874
C	-1.001706	6.325578	3.839587
C	-1.822171	7.307217	4.373559
H	-1.663776	7.763321	5.338194
C	-2.908103	7.662319	3.553430
H	-3.639621	8.412667	3.817947
C	-2.929601	6.939628	2.389945
H	-3.643470	7.008880	1.583236
C	4.599605	2.739125	11.310202
C	5.700055	3.365336	11.898288
H	6.113838	4.256125	11.439717
C	6.260707	2.863130	13.066546
H	7.106786	3.366340	13.517603
C	5.725240	1.726736	13.663504
H	6.156960	1.337224	14.576782
C	4.632010	1.091662	13.082477
H	4.206070	0.210489	13.545680
C	4.074189	1.595523	11.914613
H	3.218855	1.102491	11.467045
C	1.739807	1.552617	-1.519337
C	2.979512	1.633801	-2.154918
H	3.880583	1.725157	-1.559383
C	3.067835	1.602994	-3.542211
H	4.037592	1.663468	-4.020913
C	1.915029	1.500987	-4.313495
H	1.983737	1.484098	-5.394495
C	0.674707	1.416557	-3.689508
H	-0.226862	1.332786	-4.283433
C	0.589103	1.438366	-2.302656
H	-0.380405	1.374217	-1.822431
N	2.920110	4.220901	7.574264
N	2.055564	4.542544	6.590169
N	0.963657	4.827639	3.912639
N	0.606857	4.454493	2.675059
F	2.945936	6.952843	8.045774
F	1.354343	5.914763	9.107825
F	0.920227	7.691118	7.962609
S	4.071983	2.702742	5.684983
S	4.716780	2.528652	8.569419
S	2.183615	2.326176	3.095331
S	1.079749	3.328711	0.413800
S	-1.626164	5.840437	2.282281

[Cu(TTFASBZ)]¹⁺, S = 1/2, UKS

Cu	1.584019	2.870259	4.731666
C	3.332424	2.319628	7.054117
C	5.107253	3.129241	9.108346
H	6.106995	3.353091	8.734881
H	4.433013	3.924017	8.794973
C	1.523602	5.198716	6.505198
C	2.004656	5.985828	7.730120
C	0.534661	5.799828	5.734964
H	0.210136	6.764292	6.073406
C	-0.081751	5.334047	4.549625
C	0.204578	2.896035	2.115966
C	0.301103	1.293389	-0.270222
H	0.693882	0.679164	0.539606
H	-0.483481	0.729342	-0.776275
C	-1.209407	6.153834	4.049365
C	-1.962367	7.018033	4.822655
H	-1.813840	7.133332	5.886147
C	-2.956156	7.720664	4.105073
H	-3.640322	8.424842	4.558755
C	-2.961890	7.390548	2.777945
H	-3.616557	7.762694	2.005209
C	5.119918	2.984858	10.603456
C	6.323286	2.923021	11.307426
H	7.259102	2.947014	10.759879
C	6.337842	2.847143	12.698096
H	7.283781	2.805146	13.225650
C	5.143257	2.825308	13.407153
H	5.150777	2.768594	14.489484
C	3.934820	2.876501	12.714324
H	2.997923	2.860974	13.258584
C	3.924023	2.950885	11.328496
H	2.983591	2.993392	10.792343
C	1.382632	1.658159	-1.252600
C	2.680242	1.959337	-0.825977
H	2.901896	1.962355	0.234903
C	3.679697	2.243921	-1.748312
H	4.679932	2.468939	-1.397623
C	3.405361	2.235630	-3.113142
H	4.189660	2.452184	-3.828714
C	2.117305	1.946751	-3.548669
H	1.889582	1.936284	-4.608586
C	1.117852	1.663149	-2.623741
H	0.117870	1.430573	-2.973209
N	2.953716	3.541320	7.201724
N	2.059561	4.002985	6.271826
N	0.332291	4.220361	3.943898
N	-0.179993	3.983746	2.702811
F	3.325296	6.265248	7.681827
F	1.767222	5.351685	8.898502
F	1.384935	7.187844	7.840656
S	2.802149	1.221582	5.819546
S	4.492084	1.630793	8.222727
S	1.297692	1.720643	2.767671
S	-0.582513	2.697593	0.519997
S	-1.785766	6.195264	2.408338

[Cu(TTFASBZ)]²⁺, S = 0, RKS

Cu	2.001082	3.059021	4.565290
C	3.611432	2.591658	7.078335
C	5.166405	3.407369	9.344968
H	6.156485	3.763119	9.052996
H	4.426176	4.148914	9.038637
C	1.671127	5.376828	6.533998
C	1.974532	6.105536	7.843900
C	0.625658	5.921836	5.781308
H	0.154699	6.782632	6.217575
C	0.057855	5.476873	4.557077
C	0.609791	3.373774	1.883567
C	0.312663	1.835143	-0.514307
H	0.606206	1.237477	0.355062
H	-0.647125	1.477193	-0.892463
C	-1.274234	6.027279	4.214757
C	-2.097119	6.769347	5.044303
H	-1.833022	7.008273	6.063328
C	-3.328875	7.147627	4.462531
H	-4.085822	7.719096	4.986165
C	-3.458710	6.690189	3.180125
H	-4.293544	6.826701	2.508547
C	5.117907	3.143766	10.817045
C	6.288679	3.033401	11.573554
H	7.246864	3.120587	11.072746
C	6.245347	2.825756	12.949871
H	7.169454	2.743151	13.512022
C	5.021698	2.719942	13.601150
H	4.981555	2.559115	14.672889
C	3.844896	2.815093	12.857634
H	2.884462	2.730288	13.354143
C	3.892012	3.016306	11.485338
H	2.976819	3.087993	10.910120
C	1.359657	1.746618	-1.588393
C	2.716694	1.890773	-1.272632
H	2.991492	2.072499	-0.239258
C	3.685790	1.805898	-2.262396
H	4.730794	1.918856	-1.995639
C	3.325360	1.579105	-3.590414
H	4.085175	1.520185	-4.361727
C	1.982891	1.429178	-3.915422
H	1.686501	1.249113	-4.943348
C	1.012258	1.507141	-2.919060
H	-0.034717	1.386230	-3.178951
N	3.191814	3.805206	7.223445
N	2.360645	4.276360	6.235954
N	0.698894	4.597888	3.789966
N	0.164319	4.389838	2.557163
F	3.274359	6.476156	7.962506
F	1.670470	5.391013	8.957130
F	1.277629	7.274855	7.980737
S	3.228555	1.436190	5.865666
S	4.735947	1.928046	8.326587
S	1.634115	2.107914	2.433364
S	0.069292	3.522259	0.153012
S	-2.075712	5.787402	2.679760