Electronic Supplementary Material (ESI) for Dalton Transactions.

Discrimination of chiral copper(II) complexes upon binding of galactonoamidine ligands

Susanne Striegler* and Jessica B. Pickens
University of Arkansas, Department of Chemistry and Biochemistry, 345 N Campus Drive, Fayetteville, AR 72701, USA

*Corresponding author, phone: +1-479-575-5079; fax: +1-479-575-4049;
e-mail: Susanne.Striegler@uark.edu

Content: **1**

Binding constants for the speciation data of Cu_2bpdpo (**2**) and galactonoamidine (**1**)

The complex formation was characterized by the following general equilibrium:

$$p\,\mathrm{M} + q\,\mathrm{L} + r\,\mathrm{C} + r\,\mathrm{H} \rightleftharpoons \mathrm{M}_p\mathrm{L}_q\mathrm{C}_r\mathrm{H}_s$$

$$\beta = \frac{\mathrm{M}_p\mathrm{L}_q\mathrm{C}_r\mathrm{H}_s}{[\mathrm{M}]^p[\mathrm{L}]^q[\mathrm{C}]^r[\mathrm{H}]^s},$$

where M refers to the metal ion and L to the non-protonated ligand. The corresponding binding constants [$\beta(M_pL_qC_rH_s) \equiv \beta_{pqrs}$] were calculated using the computer program Specfit. The ligand protonation and complex formation constants were calculated from 2-4 independent titration experiments with 40-50 data points each.

Logarithmic formation constants for Cu_2bpdpo of galactonoamidine **1** (T = 303K, I = 0.1 M ($NaClO_4$); β_{pqrs} = $[M_pL_qC_rH_s]/[M]^p\,[L]^q\,[C]^r\,[H]^s$ with calculated standard deviation. The formation constants of the metal complex were previously determined by T. Gajda, M. S. Jancsó, H. Lönnberg and H. Sirges, *J. Chem. Soc., Dalton Trans.* **2002**, 1757-1763; and S. Striegler and M. Dittel, *J. Am. Chem. Soc.*, **2003**, *125*, 11518-11524 and kept fixed during the calculation here.

pqrs	$\beta_{pqrs} \pm \Delta\beta_{pqrs}$
0100	0
0101	12.3824
0102	21.9798
0103	29.2228
0104	34.3746
1100	15.2400
2100	23.3355
210-1	16.0386
210-2	4.7476
210-3	-7.93647
211-1	19.4770 ± 0.04181
211-2	12.7233 ± 0.03286
211-3	3.0797 ± 0.05095
211-4	-8.8437 ± 0.15302
211-5	-22.1596 ± 0.19042

Coordinates (Å) and energies of a complex derived from *S*-3 and galactonoamidine 1, species I:

- **Gas phase**
  Total Energy = -5151.577763223Eh; -3,232,663.828 kcal/mol
  Standard thermodynamic quantities at 298.180 K and 1.000 ATM:
  - This Molecule has 0 Imaginary Frequencies
  - Zero point vibrational energy: 426.591 kcal/mol
  - Total Enthalpy: 452.667 kcal/mol
  - Total Entropy: 243.922 cal/mol K
- **COSMO (Solvent = water)**
  Total Energy =-5151.661192258 Eh; -3232716.180 kcal/mol
  Total energy + OC corr. = -5151.658306582 Eh
  Dielectric energy = -0.095890678 Eh
  Dielectric energy + OC corr. = -0.093005002 Eh

α-spin:	*β-spin:*
E = -0.056 Eh (LUMO)	E = -0.100 Eh (LUMO)
E = -0.188Eh (HOMO)	E = -0.185 Eh (HOMO)

Coordinates (Å)

ATOM	X	Y	Z
N	-2.735562	0.651107	2.634386
C	-3.438256	1.926598	2.701904
C	-2.781480	3.138379	1.928590
C	-1.520456	2.678191	1.205959
C	-1.880757	1.380225	0.442982
C	-2.043608	0.362507	1.570879
H	-3.441555	2.206004	3.766235
H	-2.848358	1.540801	-0.052939
H	-0.833905	-1.258159	3.429801
C	-4.914881	1.727295	2.305176
H	-2.519452	3.921441	2.654432
H	-0.716561	2.466801	1.913744
O	1.324709	1.219510	0.754344
H	0.201530	-7.519175	0.574209
H	-5.346494	0.925494	2.914810
H	-4.994081	1.434655	1.255747
O	-5.680362	2.937656	2.423077
O	-3.595691	3.705144	0.899220
H	-1.801617	4.120986	-0.052757
O	-1.012461	3.698706	0.338961
H	-0.142101	-7.862706	2.270282
H	-1.547392	-5.773513	0.291422
H	-5.769361	3.151743	3.365435
H	-4.482308	3.849004	1.289409
H	3.340435	4.462843	-2.177937
C	0.403463	-7.187623	1.598118
N	-1.347528	-0.798452	1.425112
H	-2.292702	-3.453347	0.699322
H	1.471010	-7.328336	1.798850
C	-1.392913	-1.689110	2.584409
H	-2.432052	-1.743627	2.935088

H	1.385626	-5.378788	3.402625
C	-0.886441	-3.082768	2.287224
C	-1.481884	-3.871373	1.290554
C	-1.056835	-5.179860	1.060085
C	-0.019417	-5.753040	1.813071
C	0.582368	-4.961450	2.799334
C	0.152372	-3.651857	3.035882
H	0.614963	-3.072248	3.833687
H	2.294988	-4.092685	-2.766875
H	-1.967599	4.195671	-4.711755
Cu	0.586350	2.210183	-0.688596
O	-0.939360	1.001006	-0.543290
Cu	0.093300	-0.622232	0.132276
H	-0.038452	-1.256869	-5.032727
H	2.946915	-0.139792	2.441272
H	3.454491	1.282087	-1.050311
H	4.419883	0.252364	1.572679
C	2.684401	1.422142	0.992402
C	3.339035	0.102077	1.445611
H	2.827852	2.148740	1.815903
H	3.929058	-1.838745	0.713714
C	3.355929	2.034973	-0.260867
H	4.355010	2.436485	-0.042405
H	2.411993	3.874234	-0.148787
C	3.135838	-1.102055	0.515602
H	1.696121	-2.138775	1.582678
H	3.245770	-0.807264	-0.533495
N	1.819582	-1.791285	0.631253
H	1.417445	-3.303577	-4.971427
H	2.705674	-3.493225	-0.329687
C	1.752506	-2.946887	-0.288164
H	0.994419	-3.637453	0.096148
H	-0.528744	-0.080655	-2.858118
C	1.671219	-3.206389	-2.832586
C	1.178653	-2.764441	-4.059365
C	0.373125	-1.624981	-4.098976
C	0.098899	-0.964738	-2.905879
N	0.581870	-1.388478	-1.726357
C	1.343844	-2.497044	-1.676463
N	2.444737	3.085766	-0.796774
C	2.702764	3.571006	-2.167702
H	3.250585	2.786366	-2.703373
H	-1.677924	2.713131	-2.700017
C	1.324039	4.690191	-4.007167
C	0.106868	4.827400	-4.673719
C	-1.003417	4.112067	-4.222131
C	-0.855235	3.289776	-3.110931
N	0.319362	3.158528	-2.471914
C	1.399179	3.837745	-2.906366
H	2.203655	5.237287	-4.332978
H	0.025365	5.488690	-5.531065

Coordinates (Å) and energies of a complex derived from *S*-3 and galactonoamidine 1, species II:

- **Gas phase**
  Total Energy = -5151.537642881 Eh; -3232638.652 kcal/mol
  Standard thermodynamic quantities at 298.180 K and 1.000 ATM:
  - This Molecule has 0 Imaginary Frequencies
  - Zero point vibrational energy: 425.825 kcal/mol
  - Total Enthalpy: 452.296 kcal/mol
  - Total Entropy: 249.181 cal/mol K

- **COSMO (Solvent = water)**
  Total Energy = -5151.616086340 Eh; -3232687.876 kcal/mol
  Total energy + OC corr. = -5151.613003974 Eh
  Dielectric energy = -0.085414296 Eh
  Dielectric energy + OC corr. = -0.082331930 Eh

α-spin:	*β-spin:*
E = -0.049 Eh (LUMO)	E = -0.096 Eh (LUMO)
E = -0.195Eh (HOMO)	E = -0.207Eh (HOMO)

Coordinates (Å)

ATOM	X	Y	Z
N	-3.063374	0.515549	2.375397
C	-3.615266	1.827100	2.687042
C	-2.973858	3.086970	2.005902
C	-1.639341	2.725143	1.367165
C	-1.867794	1.513783	0.436953
C	-2.263374	0.361999	1.363934
H	-3.473459	1.952035	3.772034
H	-2.743150	1.747969	-0.190032
H	-1.822694	-1.701401	3.001281
C	-5.139728	1.775303	2.439483
H	-2.811982	3.854545	2.776011
H	-0.899168	2.466629	2.128401
O	1.394102	1.716959	1.470135
H	0.398446	-7.260542	-0.544368
H	-5.585431	0.980109	3.047634
H	-5.331079	1.548502	1.388440
O	-5.769203	3.038147	2.680019
O	-3.752563	3.642944	0.944906
H	0.694656	-0.659292	3.635177
O	-1.083804	3.837187	0.656143
H	-0.308856	-7.924316	0.928245
H	-1.698081	-5.773421	-0.726056
H	-5.787733	3.201181	3.636130
H	-4.607897	3.897156	1.342475
H	3.662666	4.482532	-1.657611
C	0.322732	-7.115205	0.539030
N	-1.693073	-0.850515	1.080539
H	-2.720739	-3.613896	-0.114115
H	1.320064	7.245937	0.971055
C	-2.073586	-1.958497	1.963294
H	-3.167906	-2.052508	1.950057
H	1.016073	-5.426551	2.584978

C	-1.425766	-3.266832	1.574564
C	-1.889564	-3.999895	0.472114
C	-1.312672	-5.220761	0.128082
C	-0.259042	-5.763317	0.880421
C	0.204718	-5.029089	1.979233
C	-0.370223	-3.801931	2.321275
H	0.009279	-3.255939	3.181666
H	2.700521	-3.950332	-2.621766
H	-0.951402	3.135694	-5.071884
Cu	0.730024	2.393924	-0.204470
O	-0.779399	1.227916	-0.405950
Cu	-0.255061	-0.810463	-0.161152
H	-0.603552	-2.592230	-5.042711
H	3.782859	-0.101512	1.616293
H	4.269309	3.306939	0.760242
H	4.485459	0.963102	0.421396
C	2.791524	1.829048	1.516827
C	3.525995	0.625185	0.836813
H	3.114883	1.811127	2.569776
H	3.513802	-0.666439	-0.876272
C	3.201842	3.233015	1.002567
H	2.991581	3.952433	1.797931
H	1.977915	4.567059	-0.001293
C	2.770417	-0.134688	-0.268495
H	1.812921	-1.195202	1.258914
H	2.255355	0.551921	-0.950819
N	1.787216	-1.145345	0.232517
H	1.453217	-4.014219	-4.789065
H	3.043724	-2.756531	-0.429222
C	1.981865	-2.479655	-0.362434
H	1.490065	-3.214694	0.286233
H	-1.311109	-1.168605	-3.107330
C	1.806587	-3.351438	-2.767270
C	1.109330	-3.384163	-3.974055
C	-0.032429	-2.595571	-4.120488
C	-0.431668	-1.802466	-3.049920
N	0.237812	-1.774915	-1.885955
C	1.339312	-2.539212	-1.734890
N	2.365790	3.639610	-0.167567
C	2.997623	3.623629	-1.500633
H	3.618258	2.721851	-1.566555
H	-1.088835	2.276245	-2.693232
C	2.085483	4.072567	-3.856395
C	1.046775	3.919744	-4.775867
C	-0.123441	3.268652	-4.383753
C	-0.217045	2.796183	-3.077699
N	0.782780	2.949222	-2.197099
C	1.920893	3.566865	-2.568720
H	3.006330	4.577269	-4.131909
H	1.149346	4.308975	-5.784553
H	1.188801	0.357189	2.555330
O	1.420650	-0.490055	3.017625
H	-1.834649	4.240467	0.179928

Coordinates (Å) and energies of a hypothetical assembly derived from complex *S*-3 and galactonoamidine 1 with two binding sites

- **Gas phase**
  Total Energy = -5151.567309033 Eh; -3232657.268 kcal/mol
  Standard thermodynamic quantities at 298.180 K and 1.000 ATM:
    - This Molecule has 0 Imaginary Frequencies
    - Zero point vibrational energy: 426.388 kcal/mol
    - Total Enthalpy: 452.137 kcal/mol
    - Total Entropy: 241.395 cal/mol K
- **COSMO (Solvent = water)**
  Total Energy = -5151.650294119 Eh; -3232709.342 kcal/mol
  Total energy + OC corr. = -5151.647197301 Eh
  Dielectric energy = -0.096427897 Eh
  Dielectric energy + OC corr. = -0.093331079 Eh

α-spin:	*β-spin:*
E = -0.056 Eh (LUMO)	E = -0.116 Eh (LUMO)
E = -0.183Eh (HOMO)	E = -0.179Eh (HOMO)

Coordinates (Å)

ATOM	X	Y	Z
N	-1.343723	-1.918304	-2.806689
C	-2.109481	-1.303609	-3.873669
C	-2.456917	0.193157	-3.729833
C	-2.652538	0.604085	-2.271009
C	-1.426918	0.209836	-1.442565
C	-1.071436	-1.281325	-1.705359
H	-3.077732	-1.830397	-3.954329
H	-0.580028	0.810581	-1.813494
H	-0.291725	-3.766183	0.183207
C	-1.338872	-1.554206	-5.186371
H	-3.390010	0.397892	-4.271916
H	-3.540303	0.110102	-1.859714
O	-0.325823	0.679724	2.180750
H	-2.280091	2.398843	-2.869585
H	-1.301547	-2.631108	-5.393221
H	-0.314113	-1.196220	-5.061177
O	-1.866269	-0.830966	-6.308389
O	-1.429800	1.060963	-4.240558
H	-5.614727	6.152031	1.452931
O	-2.905802	2.008239	-2.230917
H	-4.378713	5.425976	3.505057
H	3.957792	-2.449973	-3.097246
H	-2.771113	-1.145538	-6.470536
H	-1.447072	0.928997	-5.206623
H	-3.050020	3.609796	4.597670
H	6.063136	-5.011816	-1.261279
N	-0.422150	-1.853613	-0.660548
H	1.560511	-2.058354	-2.639025
C	-3.325384	3.866716	2.472057
C	-0.032086	-3.253594	-0.754325

H	-0.623416	-3.723140	-1.551236
H	4.080462	-5.373229	0.048461
C	1.445782	-3.484996	-1.030965
C	2.114228	-2.780380	-2.045791
C	3.464670	-3.006264	-2.302102
C	4.204714	-3.939767	-1.555110
C	3.536739	-4.642671	-0.546861
C	2.178775	-4.418622	-0.289010
H	1.684936	-4.988151	0.497302
H	4.676149	0.804467	2.103915
H	-5.195921	4.921939	-0.699921
Cu	-1.835777	1.637589	1.495973
O	-1.582342	0.404766	-0.046487
Cu	-0.045219	-0.613812	0.764281
H	2.850958	3.913305	-0.268646
H	1.641810	0.430079	3.864539
C	-0.479724	0.270925	3.527031
H	-1.254226	-0.512884	3.609439
H	-1.249785	1.299939	5.314215
C	0.844077	-0.305016	4.027032
H	0.783919	-0.485852	5.107765
H	2.068260	-2.078841	3.864426
C	-0.983451	1.508627	4.272412
H	-0.218600	2.290559	4.248323
H	-2.973327	1.424984	3.737022
C	1.188300	-1.647322	3.369723
H	1.388578	-2.574289	1.573922
H	0.355508	-2.342492	3.522701
N	1.436258	-1.608334	1.894927
H	4.720658	3.149536	1.232420
H	3.504099	-1.298961	2.325104
C	2.792732	-1.122520	1.510061
H	3.113327	-1.732519	0.658317
H	1.027668	2.293855	-0.809423
C	3.890149	1.169251	1.449586
C	3.912089	2.476539	0.962240
C	2.877107	2.904717	0.130930
C	1.860475	2.000484	-0.174612
N	1.841161	0.741333	0.280054
C	2.835525	0.329954	1.082196
N	-2.159976	1.998459	3.505155
C	-2.511455	3.419776	3.663266
H	-1.578780	3.994568	3.698587
H	-3.561343	3.027018	-0.700162
C	-4.223156	4.927176	2.554096
C	-4.909743	5.327559	1.409087
C	-4.681254	4.647033	0.214372
C	-3.777876	3.589288	0.202297
N	-3.109301	3.205688	1.308327
C	5.673950	-4.162734	-1.832179
H	5.855178	-4.358150	-2.896102
H	6.269386	-3.280202	-1.564196

Coordinates (Å) and energies of the assembly derived from complex *R*-3 and galactonoamidine 1 with two binding sites

- **Gas phase**
  Total Energy = -5151.561976775 Eh; -3232653.922kcal/mol
  Standard thermodynamic quantities at 298.180 K and 1.000 ATM:
  - This Molecule has 0 Imaginary Frequencies
  - Zero point vibrational energy: 426.053 kcal/mol
  - Total Enthalpy: 451.381 kcal/mol
  - Total Entropy: 239.907 cal/mol K
- **COSMO (Solvent = water)**
  Total Energy = -5151.653408002 Eh; -3232711.296 kcal/mol
  Total energy + OC corr. = -5151.650502771 Eh
  Dielectric energy = -0.105574390 Eh
  Dielectric energy + OC corr. = -0.102669159 Eh

α-spin:	β-spin:
E = -0.060 Eh (LUMO)	E = -0.115 Eh (LUMO)
E = -0.184Eh (HOMO)	E = -0.181Eh (HOMO)

Coordinates (Å)

ATOM	X	Y	Z
N	-2.460343	-0.121751	2.444868
C	-3.652839	0.703986	2.396818
C	-3.605023	2.014782	1.566119
C	-2.178648	2.524904	1.382978
C	-1.287741	1.405911	0.831583
C	-1.390295	0.180082	1.771004
H	-3.880594	1.015963	3.430902
H	-1.667912	1.116655	-0.161080
H	0.785752	-1.878546	3.072034
C	-4.816903	-0.193820	1.930746
H	-4.187328	2.786132	2.088994
H	-1.770188	2.844654	2.349010
O	2.533242	1.694581	0.631586
H	-2.980104	3.547022	-0.035480
H	-4.960467	-1.009383	2.649458
H	-4.560780	-0.633853	0.964110
O	-6.042638	0.525786	1.716531
O	-4.129380	1.875560	0.233644
H	-0.362239	5.416697	-5.319875
O	-2.197324	3.676979	0.533563
H	2.035700	5.079221	-4.693638
H	-2.499967	-4.371722	-0.382515
H	-6.321398	0.904761	2.566799
H	-5.074343	1.660501	0.358702
H	3.658867	4.576356	-2.821779
H	-3.100607	-7.278213	1.763900
N	-0.248514	-0.556007	1.846283
H	-1.515771	-2.227870	0.367343
C	1.545487	4.127389	-2.831026
C	-0.251458	-1.674520	2.771200

H	-0.788650	-1.390649	3.688893
H	-1.336404	-6.193009	3.329182
C	-0.863484	-2.980767	2.265879
C	-1.472663	-3.097741	1.014468
C	-2.027174	-4.310996	0.596136
C	-1.991691	-5.448149	1.411634
C	-1.378762	-5.328292	2.669207
C	-0.823798	-4.119125	3.085585
H	-0.356636	-4.056448	4.067666
H	2.120077	-4.069604	-1.833698
H	-2.148335	4.636716	-3.733510
Cu	1.312072	2.837954	-0.329902
O	0.062269	1.809378	0.747651
Cu	1.277177	0.240918	0.939821
H	0.026842	-1.237463	-4.327999
H	5.651623	0.624920	0.135652
C	3.705119	1.537945	-0.148589
H	3.453970	1.091677	-1.127431
H	4.514145	3.425255	0.537716
C	4.646254	0.576831	0.573400
H	4.732251	0.876774	1.625091
H	4.911176	-1.552791	0.884532
C	4.214457	2.959760	-0.404497
H	5.061245	2.988932	-1.098420
H	3.074629	4.688656	-0.559709
C	4.174291	-0.875240	0.436902
H	2.951382	-1.401478	2.004357
H	4.124872	-1.116270	-0.629280
N	2.825671	-1.201830	1.012133
H	1.025708	-3.526409	-4.015599
H	3.071024	-3.195968	0.280160
C	2.293176	-2.426609	0.367241
H	1.503511	-2.833514	1.005741
H	0.180881	0.389927	-2.441768
C	1.675053	-3.094009	-2.004711
C	1.064522	-2.788212	-3.219991
C	0.510699	-1.519593	-3.398735
C	0.598717	-0.609908	-2.347715
N	1.184119	-0.898134	-1.175955
C	1.707186	-2.122922	-1.000295
N	3.058434	3.744746	-0.944162
C	2.969687	3.827853	-2.417526
H	3.266103	2.856997	-2.831635
H	-1.437071	3.576494	-1.569864
C	1.236764	4.749553	-4.037821
C	-0.101226	4.935912	-4.382319
C	-1.096661	4.505340	-3.504501
C	-0.718626	3.905191	-2.309818
N	0.573794	3.717702	-1.981858
C	-2.571910	-6.766645	0.951208
H	-3.275517	-6.625897	0.123873
H	-1.786536	-7.450000	0.600399