Electronic Supplementary Information for Dalton Transactions

N-methylation of macrobicycles reduces encapsulation ability

Supplementary Magnetic Data

The data include parameters from analysis of magnetic exchange, tables of the temperature-dependence of molar susceptibility χ_{mol} per Cu(II) ion, magnetic moment μ, and plots of χ_{mol} and μ *vs T*.

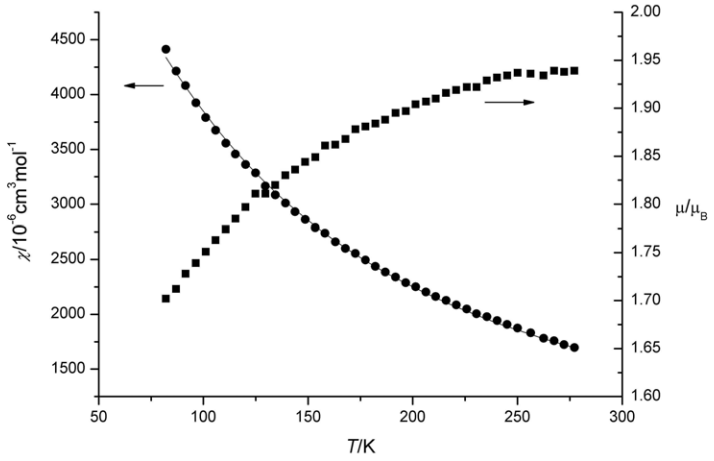
Complex 2

$[Cu_2(L^6)(CNO)_2](ClO_4)_2$ (EtOH) $(H_2O)_2$

g 2.286 +/- 0.003
-2*J* (54 +/- 1) cm^{-1}
TIP $60x10^{-6}$ cm^3mol^{-1}

T/K	$\chi_{mol}/10^{-6}$ cm^3mol^{-1}	μ/μ_B
82.1	4412	1.702
87	4213	1.712
91.5	4081	1.728
96.4	3924	1.739
101.1	3790	1.751
105.8	3673	1.763
110.7	3556	1.774
115.3	3457	1.785
120.1	3362	1.797
124.9	3285	1.811
129.6	3166	1.811
134.3	3084	1.82
139.2	3009	1.83
143.8	2932	1.836
148.6	2860	1.844
153.4	2788	1.849
158.1	2738	1.861
163	2661	1.862
167.8	2601	1.868
172.6	2554	1.878
177.4	2494	1.881
182.2	2437	1.884
186.9	2385	1.888
191.8	2340	1.895
196.7	2288	1.897
201.4	2250	1.904
206.3	2203	1.907
211	2161	1.91
215.9	2126	1.916
220.8	2086	1.919
225.8	2047	1.922
230.5	2004	1.922
235.4	1977	1.929
240.3	1942	1.932
245.1	1907	1.934
250.1	1875	1.937
256.3	1830	1.936
262.5	1782	1.934

267.5	1758	1.939
272.3	1724	1.938
277.2	1696	1.939



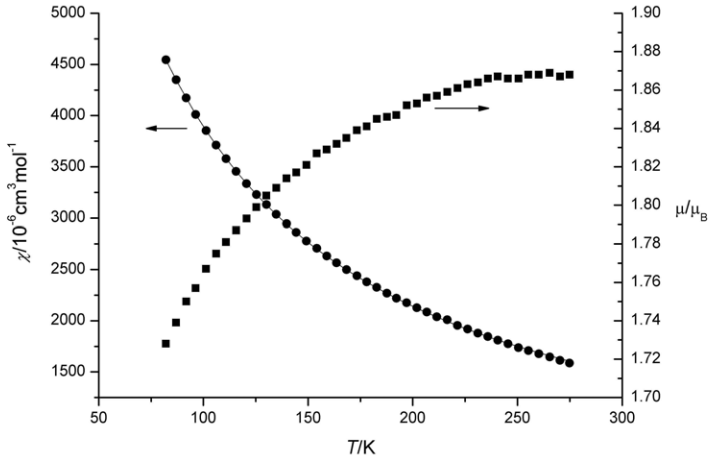
Complex 2a

$[Cu_2(L^6)(CNO)](CF_3SO_3)_3$ (EtOH)

g 2.181 +/- 0.0012
-2*J* (34.9 +/- 0.3) cm^{-1}
TIP $60x10^{-6}$ cm^3mol^{-1}

T/K	$\chi_{mol}/10^{-6}$ cm^3mol^{-1}	μ/μ_B
82.1	4545	1.728
87	4349	1.739
91.8	4173	1.75
96.3	4011	1.757
101.3	3853	1.767
106.1	3712	1.775
110.8	3578	1.781
115.6	3455	1.787
120.6	3334	1.793
125.3	3229	1.799
130.1	3130	1.805
134.8	3035	1.809
139.7	2946	1.814
144.3	2862	1.817
149.2	2778	1.821
154.1	2708	1.827
158.9	2632	1.829
163.6	2566	1.832
168.3	2500	1.835
173.3	2440	1.839
178	2380	1.841
182.8	2327	1.845
187.7	2270	1.846
192.2	2220	1.847
197.1	2175	1.852
202	2126	1.853
206.7	2084	1.856
211.5	2039	1.857
216.5	2010	1.859
221.4	1955	1.861
226.2	1918	1.863
231.1	1879	1.864
235.9	1845	1.866
240.6	1811	1.867
245.5	1774	1.866
250.5	1738	1.866
255.2	1709	1.868
260.2	1677	1.868
265.4	1646	1.869

270.3	1612	1.867
274.9	1587	1.868



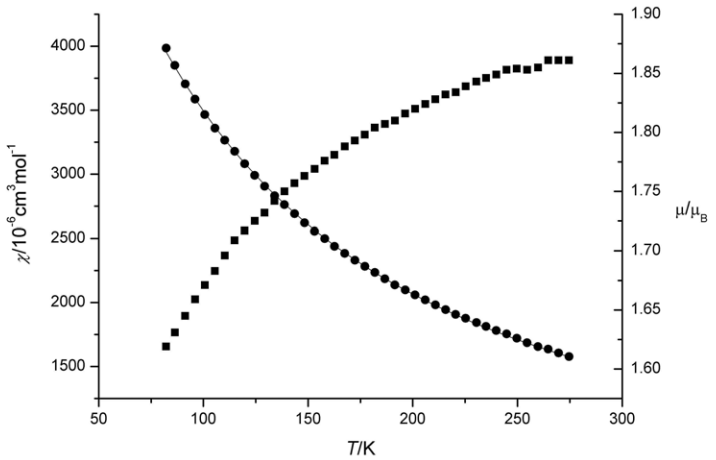
Complex 3

$[Cu_2L^6(N_3)_2]\ (ClO_4)_2.4H_2O$

g 2.20+/-0.01
-2*J* (108 +/- 1) cm^{-1}
TIP 60 x10^{-6} cm^3mol^{-1}

T/K	$\chi_{mol}/10^{-6}$ cm^3mol^{-1}	μ/μ_B
82.2	3985	1.619
86.4	3850	1.631
91.3	3705	1.645
96	3586	1.659
100.7	3465	1.671
105.5	3360	1.683
110.2	3266	1.696
114.9	3178	1.709
119.7	3081	1.717
124.5	2990	1.725
129.2	2905	1.732
134	2831	1.742
138.7	2762	1.75
143.5	2691	1.757
148.3	2620	1.763
153.1	2557	1.769
157.9	2499	1.776
162.6	2439	1.781
167.5	2385	1.788
172.3	2332	1.793
177.1	2283	1.798
181.9	2236	1.804
186.7	2186	1.807
191.5	2138	1.81
196.4	2098	1.816
201.1	2059	1.82
206	2020	1.824
210.8	1981	1.828
215.7	1945	1.832
220.5	1908	1.834
225.3	1877	1.839
230.4	1843	1.843
235	1813	1.846
239.9	1781	1.849
244.8	1754	1.853
249.7	1721	1.854
254.6	1686	1.853
259.8	1656	1.855
264.7	1636	1.861

269.6	1606	1.861
274.6	1577	1.861



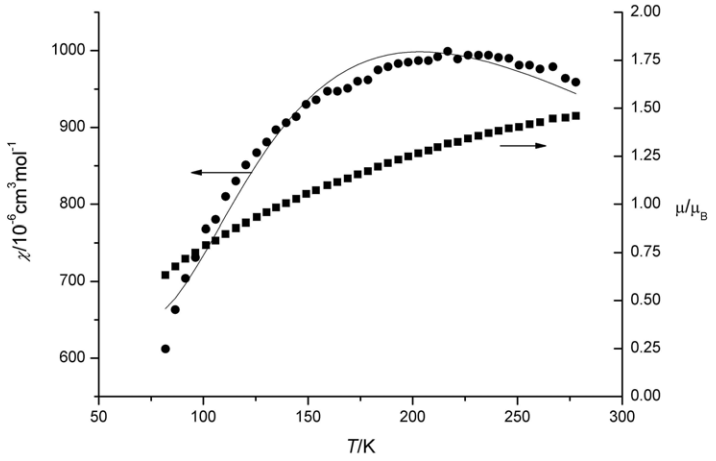
Complex 5

$[Cu_2(L^7)(CO_3)](ClO_4)_2(H_2O)$

g	2.00 +/- 0.01
-2J	(256 +/- 4) cm^{-1}
TIP	60 $cm^3\ mol^{-1}$
impurity	4.5 %

T/K	$\chi_{mol}/10^{-6}\ cm^3 mol^{-1}$	μ/μ_B
81.9	612	0.63314
86.6	663	0.67763
91.4	704	0.71736
96.2	731	0.74994
101.2	768	0.78841
105.8	780	0.8124
110.6	810	0.84645
115.5	830	0.87561
120.3	851	0.90485
125.5	867	0.93285
130.2	881	0.9578
134.7	897	0.98301
139.5	906	1.00538
144.3	914	1.02704
149.1	930	1.05308
153.8	936	1.07299
159.2	947	1.09806
164	947	1.11449
168.9	951	1.1334
173.7	960	1.15482
178.6	962	1.17222
183.4	975	1.19586
188.2	979	1.21389
193.1	983	1.2321
197.9	985	1.24859
202.7	987	1.26493
207.5	987	1.27981
211.9	992	1.29658
216.7	999	1.31581
221.5	989	1.32362
226.4	994	1.34156
231.4	994	1.3563
236.2	994	1.37029
241	991	1.38205
245.9	990	1.39533
250.8	981	1.40274
255.8	981	1.41666

260.8	976	1.42678
266.9	979	1.44559
272.9	964	1.45051
277.9	959	1.45993



Complex 6

$[Cu_3(L^7)(CO_3)](ClO_4)_4$ (MeCN)

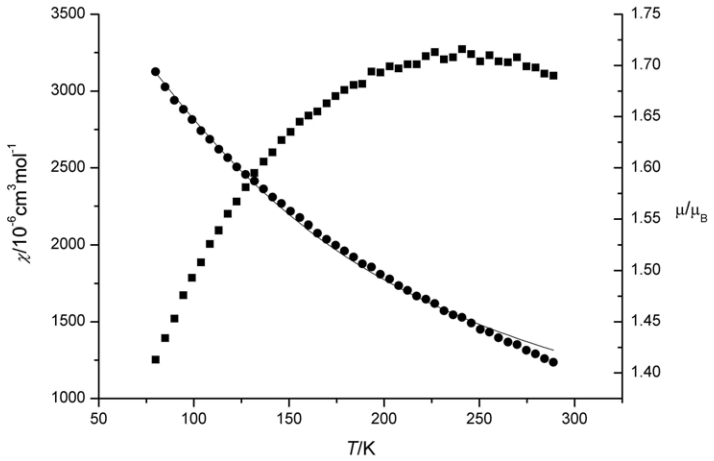
For a model in which the a single *g* value is set for each of the three Cu(II) ions:
g 2.07 +/- 0.01
-2*J* (106 +/- 2) cm^{-1}
TIP 60 x10^{-6} cm^3mol^{-1}.

For a model in which the separate *g* values are set for the dimeric and monomeric Cu(II) ion components of the model:
g(dimer) 2.10 +/- 0.01
g(monomer) 2.0 (this was set at the lowest feasible value to improve the fit in the high *T* regime).
-2*J* (102 +/- 2) cm^{-1}
TIP 60 x10^{-6} cm^3mol^{-1}

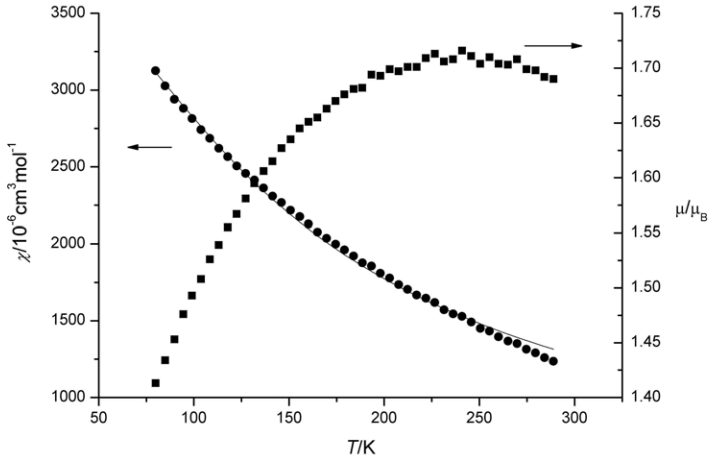
T/K	$\chi_{mol}/10^{-6}$ cm^3mol^{-1}	μ/μ_B
79.9	3126	1.413
84.9	3027	1.434
89.8	2939	1.453
94.5	2881	1.476
99	2814	1.493
103.7	2742	1.508
108.4	2685	1.526
113.1	2620	1.539
117.8	2566	1.555
122.5	2505	1.567
127.2	2457	1.581
131.8	2413	1.595
136.6	2362	1.606
141.3	2308	1.615
146	2267	1.627
150.8	2217	1.635
155.6	2176	1.645
160.2	2128	1.651
164.9	2077	1.655
169.7	2037	1.663
174.4	1999	1.67
179.1	1962	1.676
183.9	1921	1.681
188.5	1877	1.682
193.3	1857	1.694
198	1809	1.693
202.9	1779	1.699
207.6	1735	1.697
212.3	1704	1.701
217.1	1667	1.701

221.9	1647	1.709
226.6	1619	1.713
231.4	1572	1.706
236.2	1545	1.708
240.9	1528	1.716
245.7	1491	1.711
250.5	1450	1.704
255.3	1433	1.71
260.1	1396	1.704
265	1368	1.703
269.8	1351	1.708

Fit for a model in which the a single *g* value is set for each of the three Cu(II) ions:



For a model in which the separate *g* values are set for the dimeric and monomeric Cu(II) ion components of the model.



Complex 7

$[Cu_4(L^7)_2(N_3)](ClO_4)_7\ (H_2O)_6$

g 1.90 +/- 0.01
-2*J* (44 +/- 3) cm^{-1}
TIP 60 x10^{-6} cm^3mol^{-1}

T/K	$\chi_{mol}/10^{-6}$ cm^3mol^{-1}	μ/μ_B
82.1	3664	1.551
86.8	3499	1.558
91.8	3347	1.568
96.6	3211	1.575
101.3	3093	1.583
106.2	2986	1.593
111.4	2854	1.594
116.2	2765	1.603
121	2673	1.608
125.8	2581	1.611
130.6	2496	1.615
135.4	2419	1.618
140.2	2356	1.625
145	2286	1.628
149.8	2216	1.629
154.7	2157	1.634
159.3	2098	1.635
164.1	2047	1.639
169.1	1984	1.638
173.9	1929	1.638
178.8	1881	1.64
183.5	1833	1.64
188.4	1777	1.637
193.2	1737	1.638
198.2	1696	1.64
203	1649	1.636
207.8	1623	1.642
212.6	1578	1.638
217.5	1545	1.64
222.4	1508	1.638
227.3	1468	1.634
232.1	1435	1.632
237	1398	1.628
241.9	1376	1.631
246.8	1332	1.621
251.8	1309	1.624
256.6	1280	1.621
261.8	1265	1.628
266.7	1239	1.626

271.6	1199	1.614
276.3	1173	1.61