Supplementary Material (ESI) for PCCP

Electronic Supplementary Information

Natural Abundance ^{13}C and ^{15}N Solid-State NMR Analysis of Paramagnetic Transition-Metal Cyanide Systems

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Table S1 Selected Bond Lengths (Å) and Angles(°) for **8.**[a]

Zn(1) – N(1*)	2.362(17)	Zn(1) – N(3*)	2.135(9)
Zn(1) – N(3")	2.135(9)	Zn(1) – N(3')	2.135(9)
Zn(1) – N(1)	2.362(17)	Zn(1) – N(3)	2.135(9)
Au(1) – Au(2$)	3.2201(6)	Au(1) – Au(2)	3.2201(6)
N(1*) – Zn(1) – N(3*)	89.5(4)	N(1*) – Zn(1) – N(3")	89.5(4)
N(3*) – Zn(1) – N(3")	97.7(5)	N(1*) – Zn(1) – N(3')	90.5(4)
N(3*) – Zn(1) – N(3')	82.3(5)	N(3") – Zn(1) – N(3')	180
N(1*) – Zn(1) – N(1)	180	N(3*) – Zn(1) – N(1)	90.5(4)
N(3") – Zn(1) – N(1)	90.5(4)	N(3') – Zn(1) – N(1)	89.5(4)
N(1*) – Zn(1) – N(3)	90.5(4)	N(3*) – Zn(1) – N(3)	179.995
N(3") – Zn(1) – N(3)	82.3(5)	N(3') – Zn(1) – N(3)	97.7(5)
N(1) – Zn(1) – N(3)	89.5(4)	Zn(1) – N(1) – C(1)	150.4(14)
Zn(1) – N(3) – C(3)	106.4(8)		

[a]Symmetry transformations : *: 1-x, -y, 3-z; ": 1-x, y, 3-z; ': x, -y, z; $: x , y, 1+z

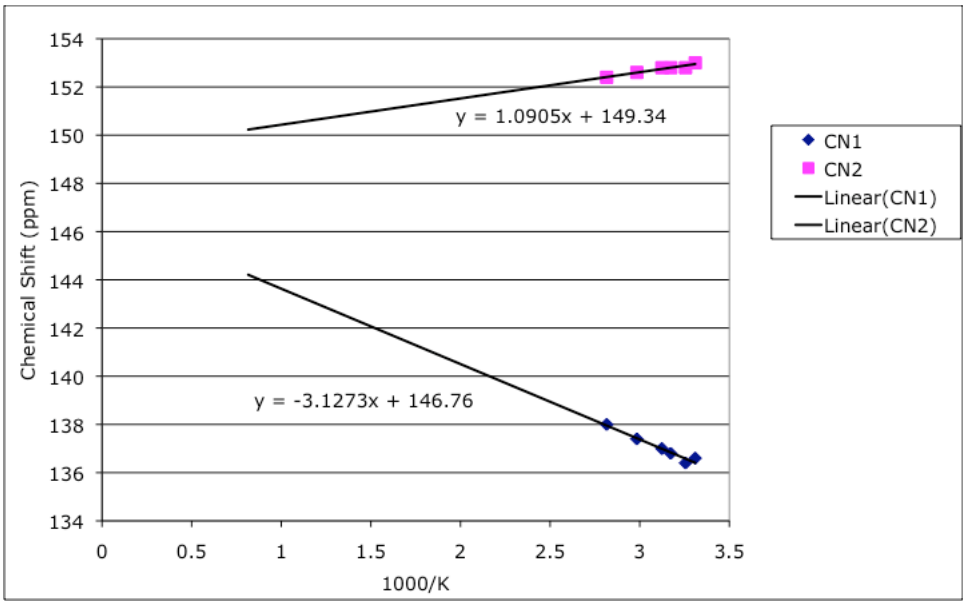

Figure S1: The temperature dependence of the two ^{13}C cyanide signals for compound **1**.

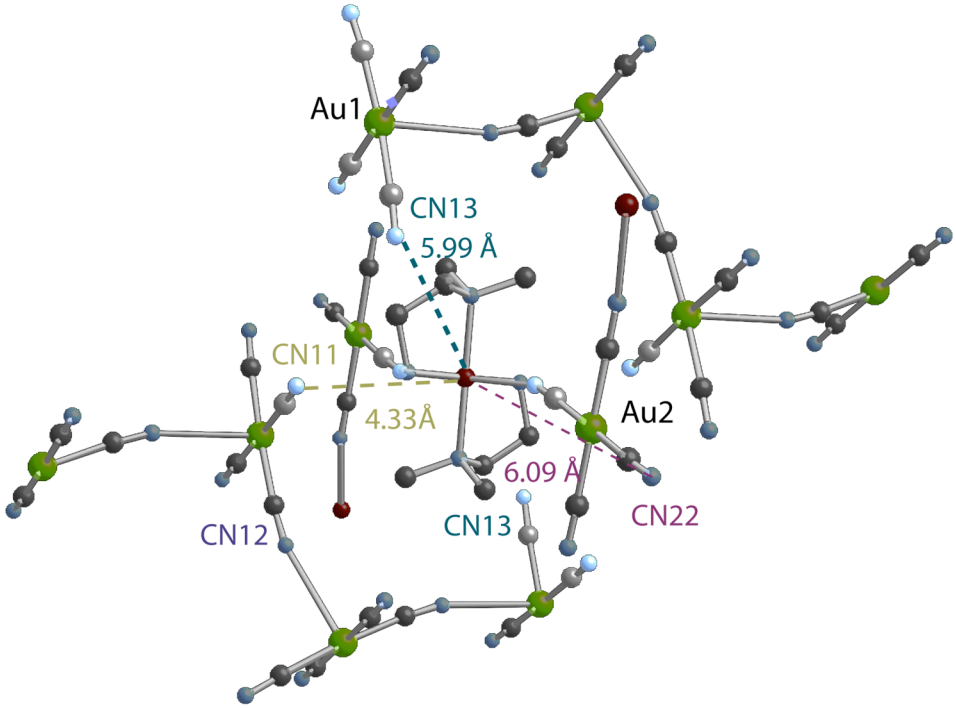

Figure S2: Structure of compound **3** along with selected nitrogen to copper distances.

Table S2: Results of ^{13}C variable-temperature experiments.

Sample				
Site	δ_{diam} (ppm)	Slope (ppm/1000 K)	^{13}C $\rho_{\alpha\beta}$ (a.u.)	R^2
$[Cu(en)_2][Hg(CN)_2Cl]_2$				
CN1	147 ± 2	-3.1273	-0.000089	0.958
CN2	149 ± 2	1.0905	0.000031	0.935
en (-CH_2-)	n.d.			
$[Cu(en)_2][Ag_2(CN)_3][Ag(CN)_2]$				
CN21	153 ± 2	-2.28749	-0.000065	0.937
CN21[a]	153 ± 2	-2.28749	-0.000065	0.937
CN11		0		
CN11[a]		0		
CN20		0		
en (-CH_2-)	43 ± 13	-108.68957	-0.003083	0.993
$[Cu(en)_2][Au(CN)_2]_2$				
CN1	152 ± 2	-8.1537	-0.000231	0.963
CN2	152 ± 2	5.7818	0.000164	0.954
en (-CH2-)	-40 ± 30	-81.009	-0.002298	0.891

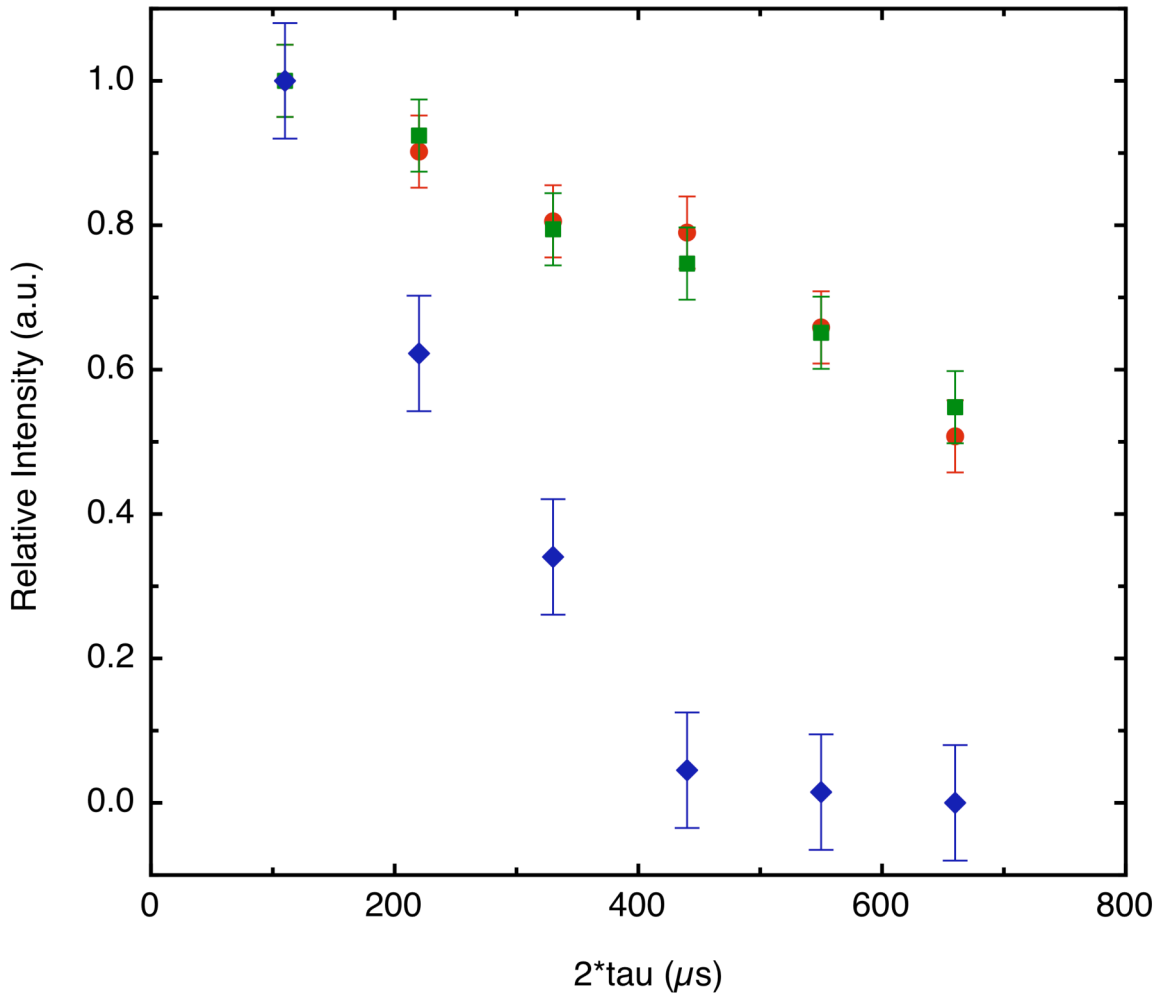

Figure S3: Spin-spin relaxation data for sample $[Cu(en)_2[Zn(NC)_4(CuCN)_2]$. The intensities for the signals at 182 (red circles) and 165 ppm (green squares) signals decay much more slowly than the 122 ppm signal (blue diamonds).

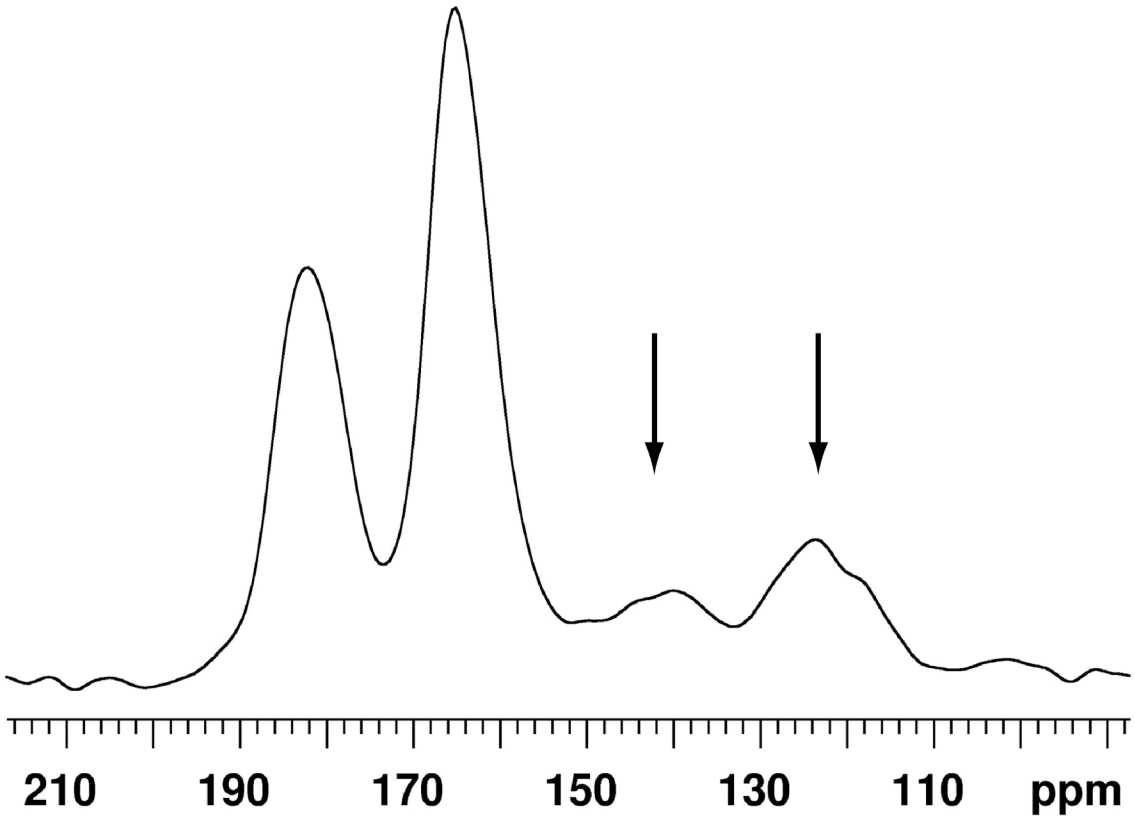

Figure S4: ^{13}C MAS of $[Cu(en)_2[Zn(NC)_4(CuCN)_2]$ showing the splitting of the low-frequency peak upon changing the temperature.

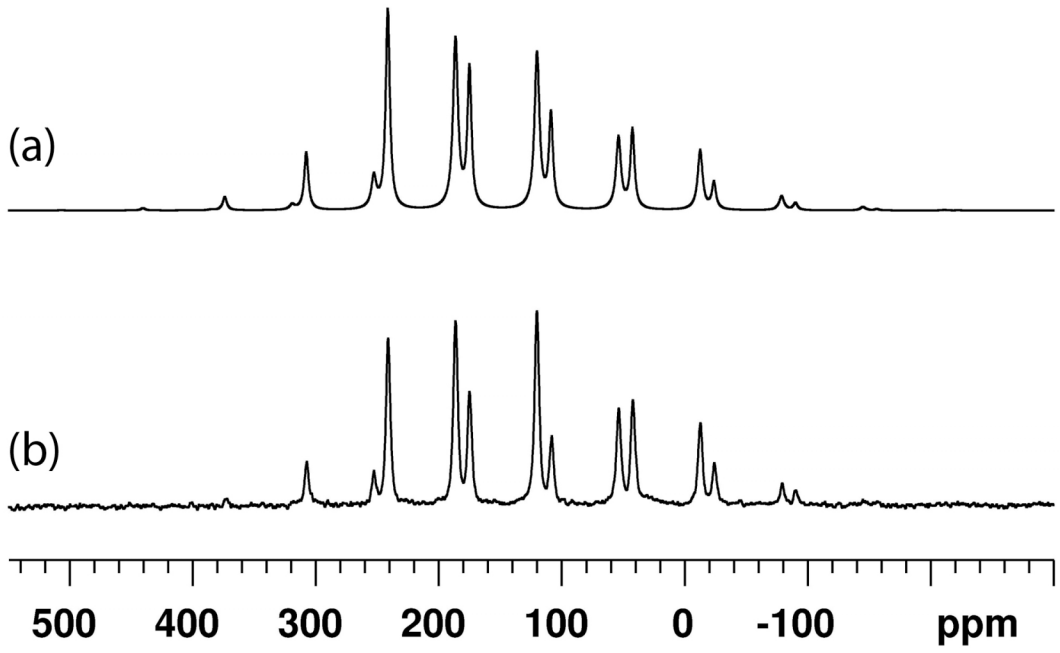

Figure S5: Simulated (a) and experimental (b) spectra for compound 7 acquired at 10 kHz spinning.

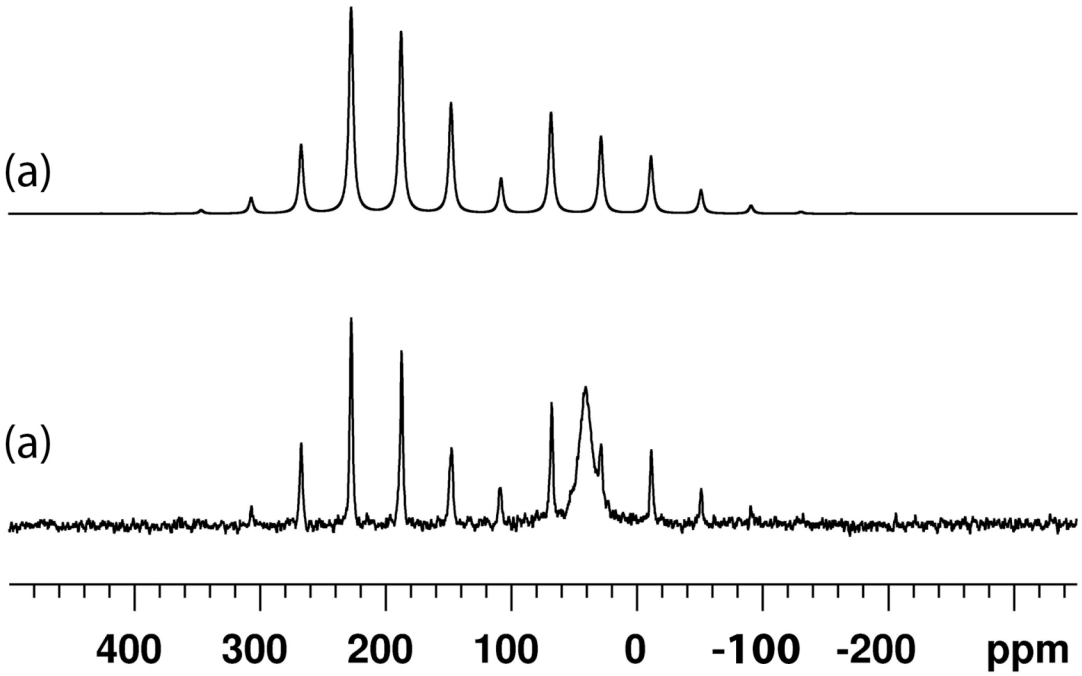

Figure S6: Simulation (a) and experimental (b) spectra for compound 8 acquired at 6 kHz spinning.