Supplementary information:

S1. Supplementary magnetic data

Complex 5, $Cu_2L^4(CF_3SO_3)_2(NO_3)_2$

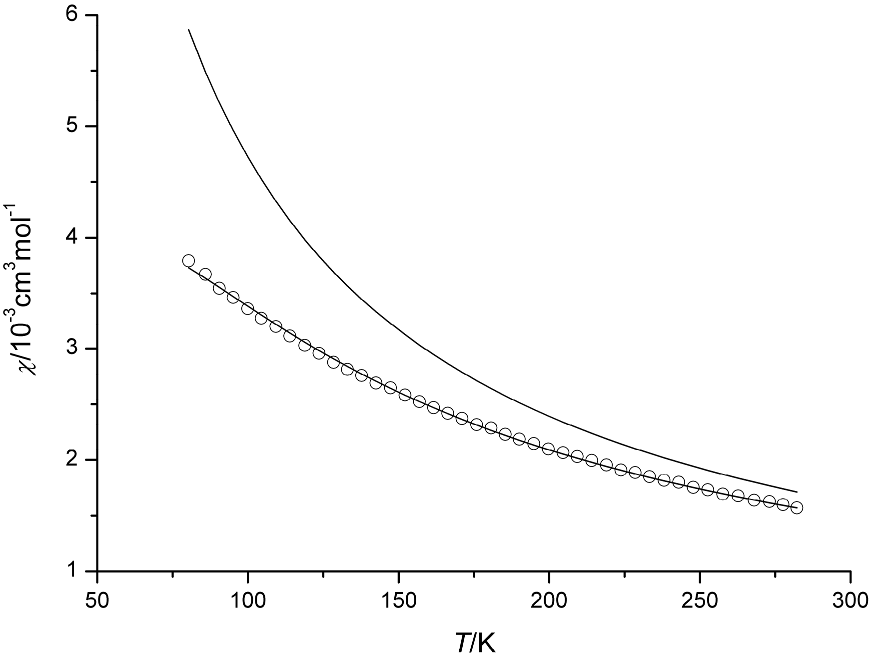


Figure S1
Magnetic behaviour of complex **5**, $Cu_2L^4(CF_3SO_3)_2(NO_3)_2$. Values of μ per Cu(II) ion (open circles) are plotted against T. Moderate antiferromagnetic exhange is evident from a comparison with the upper line which shows Curie-law behaviour. Attempts to fit the the Bleaney-Bowers equation to the data give parameters of; $-2J = 130$ cm^{-1}, $g = 1.98$ and a paramagnetic impurity of 0.30 (lower line in the Figure), whereas if no impurity is assumed the parameters are $-2J = 68$ cm^{-1}, $g = 2.23$. The temperature-independent paramagnetism was set at 60×10^{-6} cm^{3}mol^{-1} per Cu(II).

Complex 6, $Cu_2L^4(Cl_4)MeOH.2H_2O$

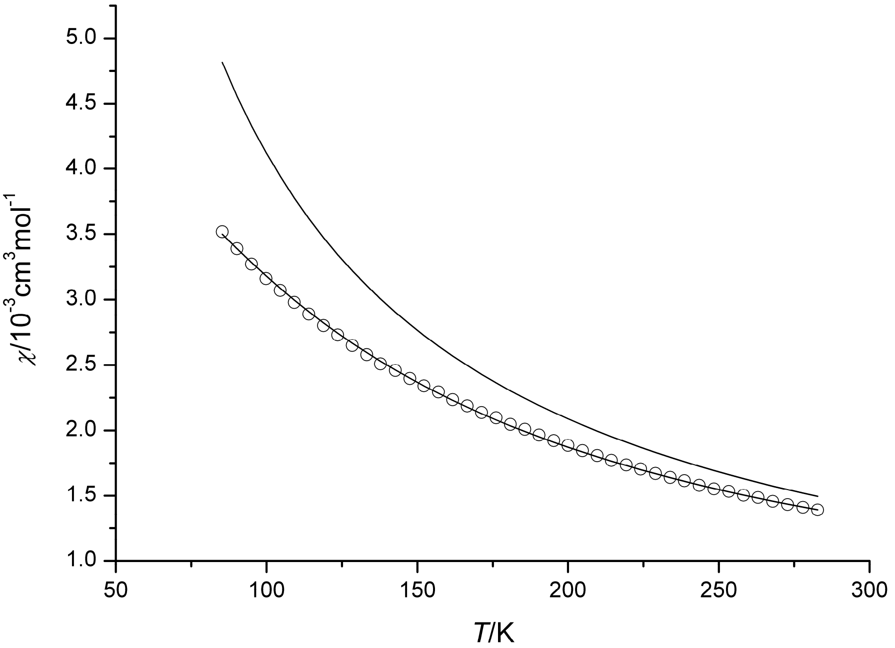


Figure S2 Magnetic behaviour of complex **6**, $Cu_2L^4(Cl_4)MeOH.2H_2O$. Values of μ per Cu(II) ion (open circles) are plotted against T. Moderate antiferromagnetic exhange is evident from a comparison with the upper line which shows Curie-law behaviour. Attempts to fit the the Bleaney-Bowers equation to the data give parameters of; $-2J = 55$ cm^{-1}, $g = 2.1$. The temperature-independent paramagnetism was set at 60×10^{-6} cm^{3}mol^{-1} per Cu(II).

Complex 8b, Cu_2L^5 $(BF_4)_3OH$

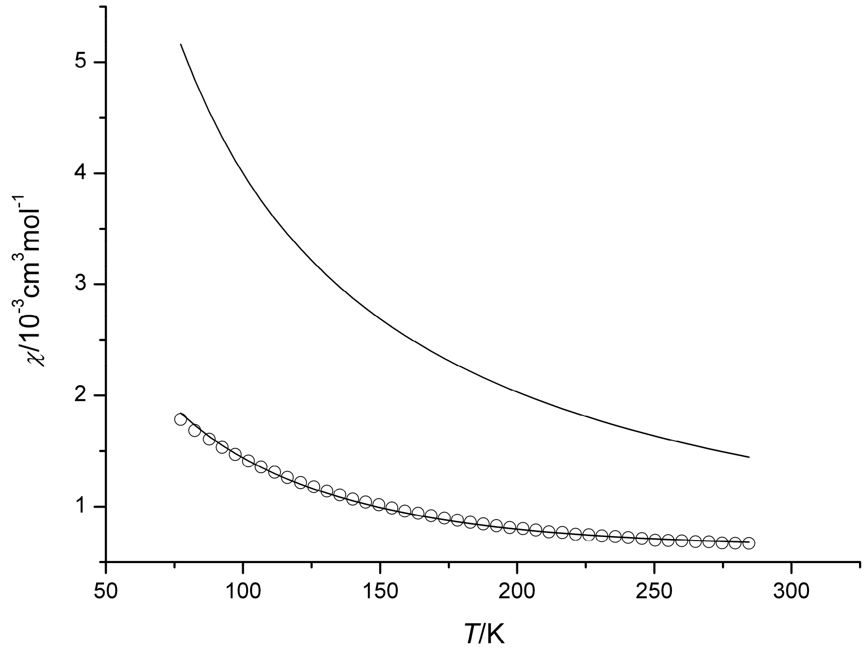
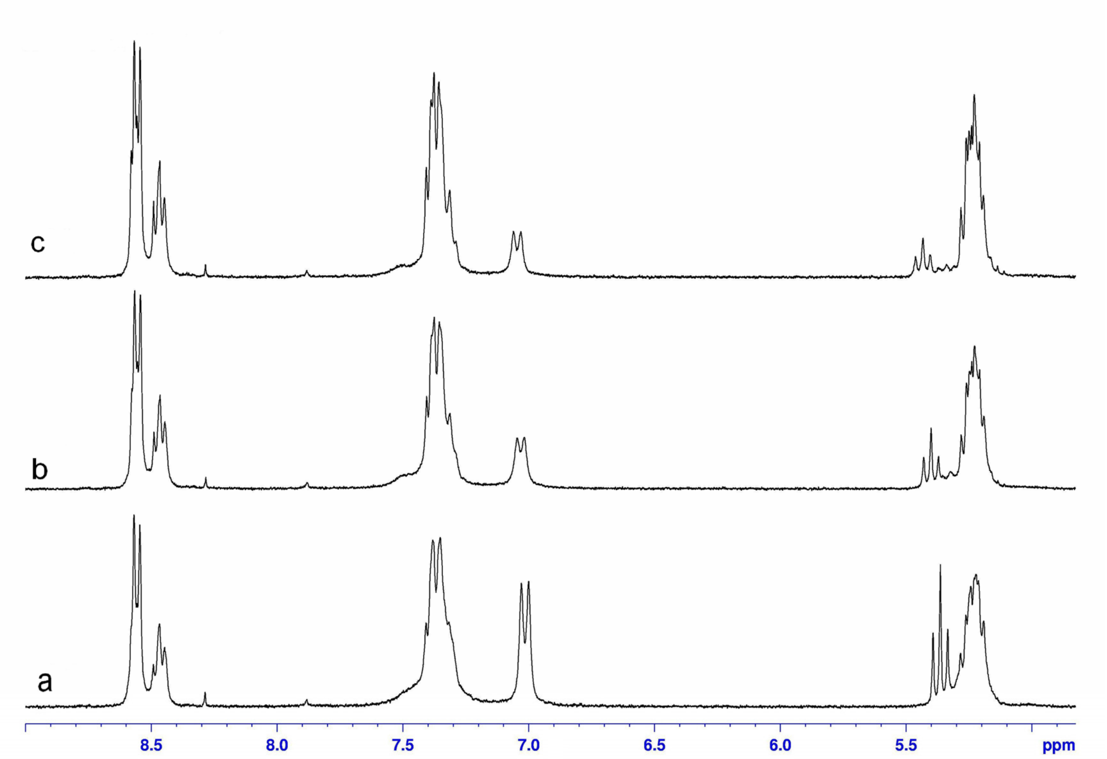


Figure S3 Magnetic behaviour of complex **8b**, Cu_2L^5 $(BF_4)_3OH$.
Values of μ per Cu(II) ion (open circles) are plotted against T. Comparison of the data with the upper line, Curie-law behaviour, shows very strong antiferromagnetic exhange. Fitting the the Bleaney-Bowers equation to the data and allowing for a paramagnetic impurity gives an exchange parameter of $-2J = 680$ cm^{-1} with $g = 2.05$ and a paramagnetic impurity of 0.17 (lower line in the Figure). In each case the temperature-independent paramagnetism was set at 60×10^{-6} cm^{3}mol^{-1} per Cu(II).

2.Nmr spectral data

Figure S4
Course of the hydrolysis reaction of 4 in D2O



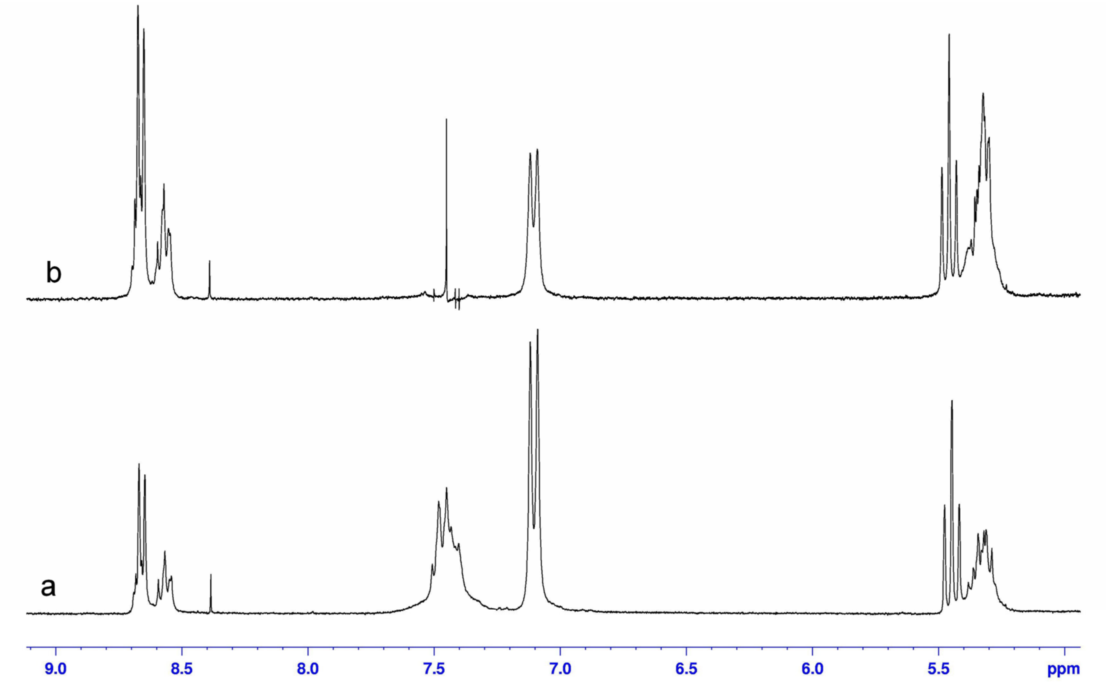
a after 1hr; b after 4 hr; c after 24hr; ≈7.0,d,ppm and ≈5.4,t,ppm signals represent remnant reactant cryptand.

TableS1: NMR Spectra of the hydrolysis product of 4 (ppm /TMS)

^{1}H resonance	Correlated ^{13}C resonance[b]	Coupling to ^{1}H resonance at:	Comment
8.6,m[a]	195	≈5.2	
8.5,m[a]	----	≈5.2	
7.4,m	164	≈5.2	1DTOCSY at 8.68 ppm selectively enhances the low field portion of this resonance, causing it to present as an approximate doublet.
5.3,m	102	≈7.4, 8.5, 8.6	Decoupling at 7.4ppm simplifies this resonance to an approximate doublet. 1DTOCSY at 8.68 ppm generates a low intensity approximate doublet of doublets
3.2,m	43,49	≈2.6	
2.6,m	40,54,58	≈2.5, 3.2	
2.5,m	58,40	≈2.6	

a both these multiplets consist of a pair of overlapped doublets, one major, one minor intensity.

b there are minor resonances at 196, and104ppm; the region 43-58 ppm contains 7 signals in total.



a ^{1}H nmr in the range 9.0-5.5ppm, standard spectrum

b ^{1}H nmr in the range 9.0-5.5ppm, irradiated at7.5ppm to decouple resonance of the neighbouring protons; the resonance at 8.5,8.6 are unaffected, but simplification of the 5.3 ppm resonance takes place, presenting a pattern closer to doublet; the remnant coupling relates to the 8.6 ppm signal.

Figure S5 Effect of irradiation at 7.5ppm on the 5.3ppm resonance

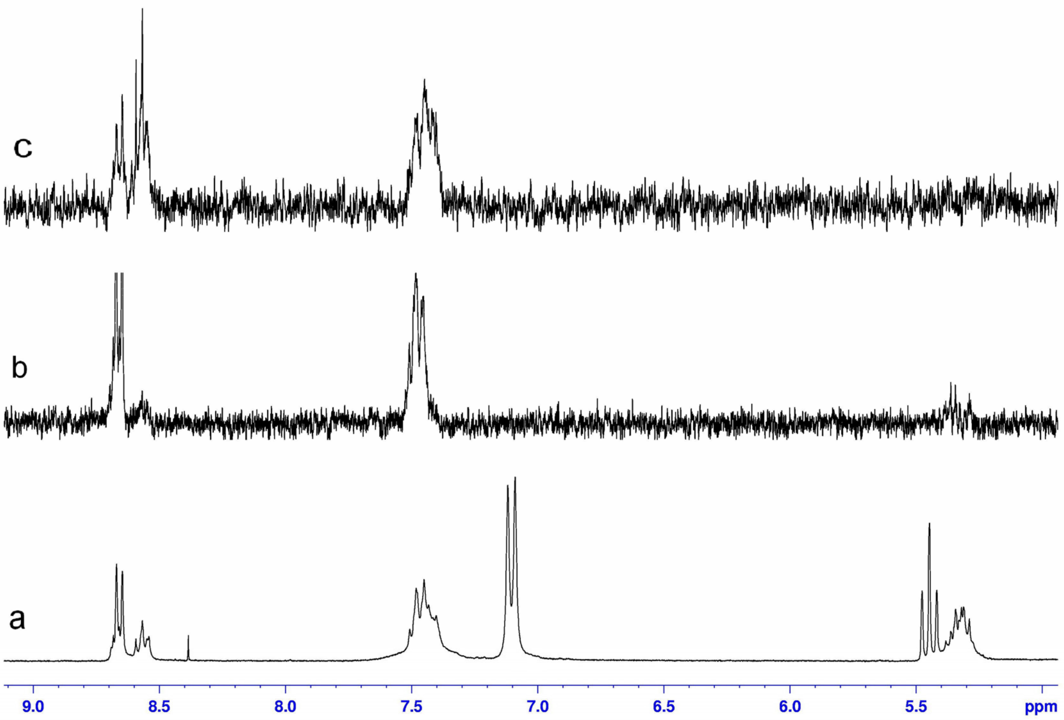


Figure S6. 1D-TOCSY spectra of hydrolysis product of 4.

TOCSY spectra with 8.54(*c*) and 8.684 (*b*) irradiationto identify the protons in the spin systems associated with the 8.5 vs 8.6 ppm resonances. Spectrum (a) is a normal ^{1}H spectrum for comparison. In *b* the lower field portion of each resonance is selected whereas in c the higher field portion of the 7.5ppm resonance is enhanced and the 5.3ppm resonance is unobserved..

Selective 1D TOCSY H-H NMR spectra were obtained on a Bruker Avance-400 MHz spectrometer operating at 400.13 MHz for protons, employing a high-resolution broad-band HX probe using shape-selective pulses. To obtain sufficient selectivity "long" selective pulses of 80ms were employed with a corresponding power level of 76dB, a mixing time of 60ms allowed sufficient magnetisation transfer to neighbouring protons.