Trans-methylpyridine cyclen *versus* cross-bridged *trans*-methylpyridine cyclen. Synthesis, acid-base and metal complexation studies (metal = Co^{2+}, Cu^{2+}, and Zn^{2+})

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Table S1. Overall protonation constants (β_i^H) of Cpy_2 and $CRpy_2$. $T = 298$ K and $I = 0.1$ mol dm^{-3} in NMe_4NO_3

Equilibrium quotient	Cpy_2 [a]	$CRpy_2$ [a]
[HL]/[L][H]	9.90(1)	13.8(1)[b]
$[H_2L]/[L][H]^2$	18.30(2)	19.11(2)
$[H_3L]/[L][H]^3$	22.06(3)	23.07(3)
$[H_4L]/[L][H]^4$	24.55(3)	25.53(8)

[a] Values in brackets are standard deviations in the last significant figure. [b] Values determined by ^1H NMR titration.

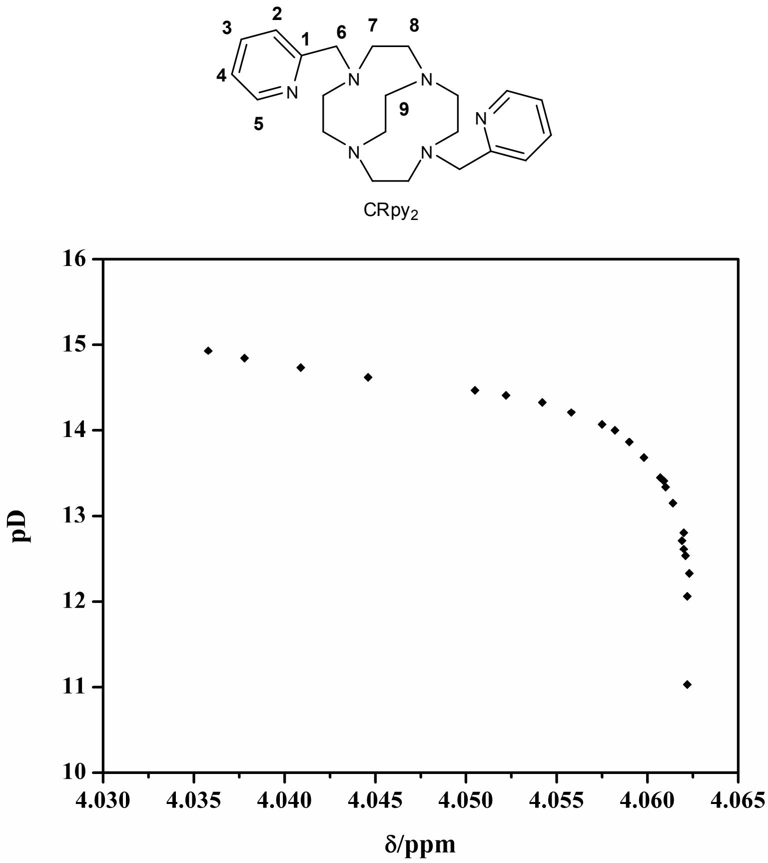


Figure S1. NMR titration curve, pD in function of the chemical shift (δ), for $CRpy_2$ following proton resonance H_6

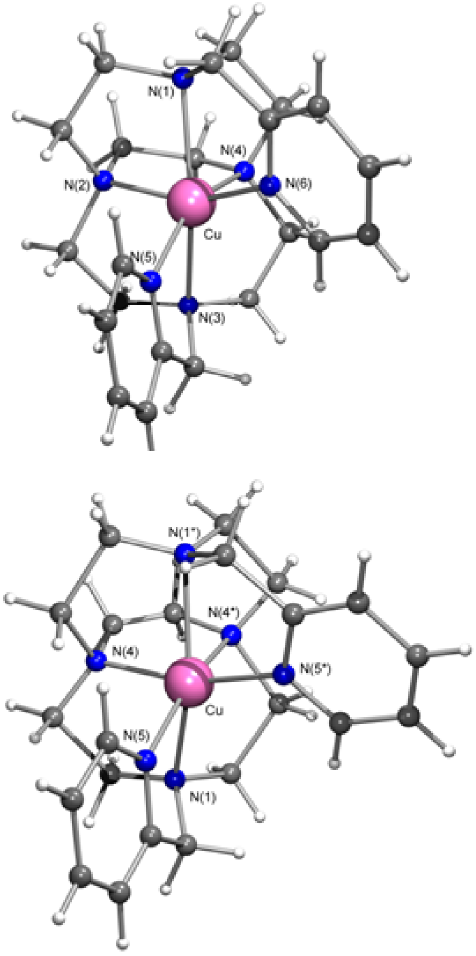


Fig. S2 Perspective view of $[CuCRpy_2]^{2+}$ showing the overall structures of the A and B molecules with a two-fold crystallographic symmetry axis, * denotes the symmetry operation: *-x*, *y*, 3/2-*z*

Crystal data:
Molecular Formula: $[C_{20}H_{30}CuN_6](ClO_4)_2$; M_w = 642.98; $C_{22}H_{32}Cl_2CuNO_8$, *Crystal dimensions 0.01 x 0.10 x 0.20, a = 33.3151(15), b = 18.5663(11), c = 17.2121(8) Å, V = 10646.3(9)* $Å^3$, *Orthorhombic , space group Pbcn, R = 0.0967 [I > 2σ(I)] and 0.2099 (all data*
CCDC 792050

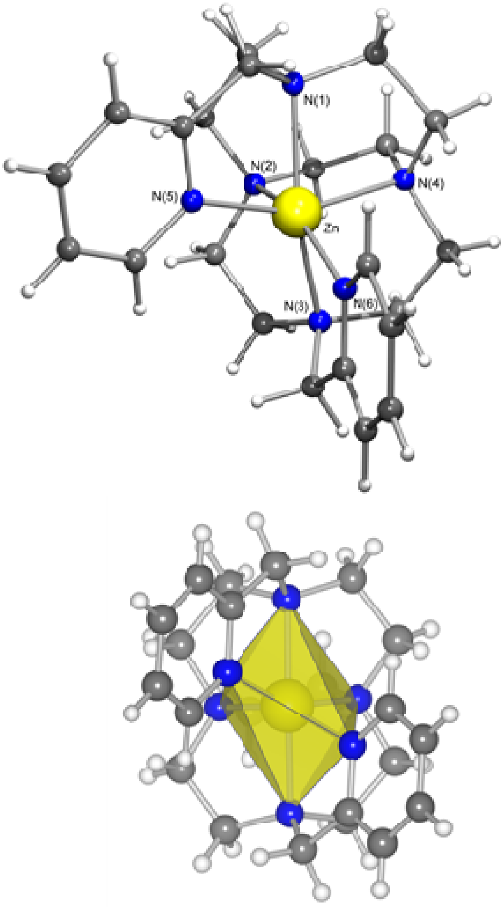


Fig. S3 Two perspective views of $[ZnCRpy_2]^{2+}$ showing the overall structure with atomic notation scheme used (top) and the zinc(II) distorted octahedral coordination sphere (bottom).

Crystal data:
Molecular Formula: $[C_{22}H_{32}N_6Zn](ZnI_4)$; M_w = 659.82; *Crystal dimensions 0.08 x 0.04 x 0.03,* $C_{22}H_{32}I_4N_6Zn_2$, *a = 14.3317(10), b = 14.7028(11), c = 14.4633(13) Å V = 2996.1(4)* $Å^3$, *β = 100.555(7)°, Monoclinic, space group* $P2_1/n$, *R= 0.0575 [I > 2σ(I)] and 0.0786 (all data)*
CCDC 778332

In spite of the X-ray data of $[ZnCRpy_2]^{2+}$ and $[CuCRpy_2]^{2+}$ complexes have not enough quality to be published their structures are unequivocally solved allowing a broad discussion of their metal coordination spheres:

These structures revealed that the complexes of copper(II) and zinc(II) with cross-bridged cyclen derivatives $CRPy_2$ adopt a N_6 coordination with a *cis*-octahedral structures in solid state with severe distortions which are imposed by the small cleft available in the macrobicycle.

The asymmetric unit of the Cu^{2+} complex with $CRpy_2$ (Figure S1) is composed of three $[CuCRpy_2]^{2+}$ cations, one with entire occupancy (A) and two with half occupancies (B and C), and four ClO_4^- counter anions with entire occupancies, which is consistent with the molecular formula

$[CuCRpy_2](ClO_4)_2$. The structure indicates that the coordination sphere of each molecule is a distorted octahedron with equatorial coordination plane defined by two pyridine nitrogen donors and two nitrogen atoms of the macrobicyclic backbone.

A molecular diagram of $[ZnCRpy_2]^{2+}$ complex from $[ZnCRpy_2](ZnI_4)$ with the labelling scheme adopted is shown in Fig. Y (S1). The four amine nitrogen atoms of the macrobicyclic framework span two continuous faces of the distorted octahedron around Zn^{2+} metal ion and the pyridine nitrogen atoms occupy the remaining *cis* positions of the coordination polyhedron, see Fig. S2 (bottom). This geometric arrangement is equivalent to that observed for $[CuCRpy_2]^{2+}$.

Table S2. EPR parameters of $[CuCpy_2]^{2+}$ and $[CuCRpy_2]^{2+}$ complexes

	$g_{\parallel}$	$g_{\perp}$	$A_{\parallel}$ (10^4 cm^{-1})
$[CuCpy_2]^{2+\,a}$	2.19	2.07	193
$[CuCRpy_2]^{2+\,a}$	2.22	2.05	140

[a] This work, in frozen solution of DMF at 150 K, $C = 10^{-2}$ mole dm^{-3}.

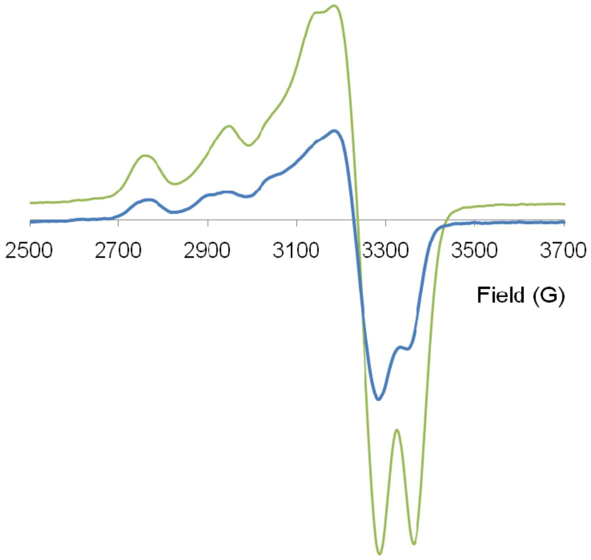
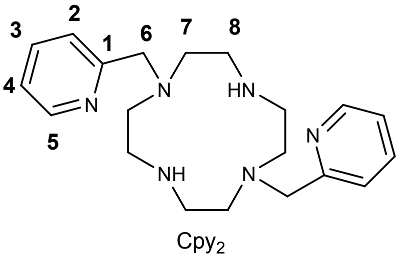


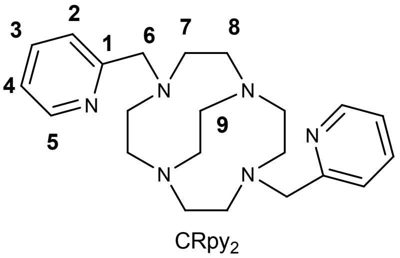
Fig. S4 EPR spectra of $[CuCpy_2]^{2+}$ at two different concentrations C and $C/2$ ($C = 10^{-2}$ mole dm^{-3},150 K in frozen DMF)

Table S3. UV/vis data of the metal complexes in DMF solution and at the solid state. λ (nm), ε ($dm^3\ mol^{-1}\ cm^{-1}$) in brackets

	Solution in DMF	Solid state
$[CuCpy_2]^{2+}$	652 (157)	648
$[CuCRpy_2]^{2+}$	712 (89)	710
$[ZnCpy_2]^{2+}$	343 (142)	341
$[ZnCRpy_2]^{2+}$	359 (146)	358
$[CoCpy_2]^{2+}$	507 (82)	505
$[CoCRpy_2]^{3+}$	475 (436)	473



Cpy$_2$



CRpy$_2$

Table S4. ^{1}H and ^{13}C NMR data for Cpy$_2$, CRpy$_2$ and their Zn(II) complexes in CD$_3$CN (10^{-2} mol dm^{-3}, 400 and 100 MHz at 298 K)

	Cpy$_2$			CRpy$_2$		
^{1}H	H$_2$	d (2H)	7.45	H$_2$	d (2H)	7.40
	H$_3$	t (2H)	7.71	H$_3$	t (2H)	7.75
	H$_4$	t (2H)	7.21	H$_4$	t (2H)	7.25
	H$_5$	d (2H)	8.50	H$_5$	d (2H)	8.54
	H$_6$	s (4H)	3.84	H$_6$	s (4H)	4.04
	H$_7$	t (8H)	2.64	H$_7$	t (8H)	2.91
	H$_8$	t (8H)	2.73	H$_8$	t (8H)	3.12
				H$_9$	s (4H)	3.08
				NH$^+$	s (1H)	12.25
^{13}C	C$_1$	2C	118.2	C$_1$	2C	118.2
	C$_2$	2C	124.3	C$_2$	2C	124.1
	C$_3$	2C	137.4	C$_3$	2C	137.5
	C$_4$	2C	123.0	C$_4$	2C	123.3
	C$_5$	2C	149.9	C$_5$	2C	150.3
	C$_6$	2C	62.5	C$_6$	2C	60.0
	C$_7$	4C	52.5	C$_7$	4C	56.6
	C	4C	46.9	C$_8$	4C	51.9
				C$_9$	2C	48.0
	[Zn(Cpy$_2$)]$^{2+}$			[Zn(CRpy$_2$)]$^{2+}$		
^{1}H	H$_2$	d (2H)	7.57	H$_2$	d (2H)	8.05
	H$_3$	t (2H)	8.05	H$_3$	t (2H)	8.61
	H$_4$	t (2H)	7.42	H$_4$	t (2H)	8.00
	H$_5$	d (2H)	8.08	H$_5$	d (2H)	8.76
	H$_6$	s (4H)	4.10	H$_6$	s (4H)	4.55
	H$_7$	m (4H); m (4H)	2.82; 2.98	H$_7$	m (8H)	3.22
	H$_8$	m (4H); m (4H)	2.89; 2.94	H$_8$	m (4H); m (4H)	2.98; 3.23
				H$_9$	s (4H)	3.15
^{13}C	C$_1$	2C	118.3	C$_1$	2C	118.3
	C$_2$	2C	126.1	C$_2$	2C	128.6
	C$_3$	2C	141.7	C$_3$	2C	143.0
	C$_4$	2C	125.4	C$_4$	2C	127.6
	C$_5$	2C	149.9	C$_5$	2C	148.8
	C$_6$	2C	56.7	C$_6$	*coalescence*	*53.8*
	C$_7$	4C	51.1	C$_7$	*coalescence*	*52.5*
	C$_8$	4C	44.2	C$_8$	4C	56.1
				C$_9$	2C	45.5

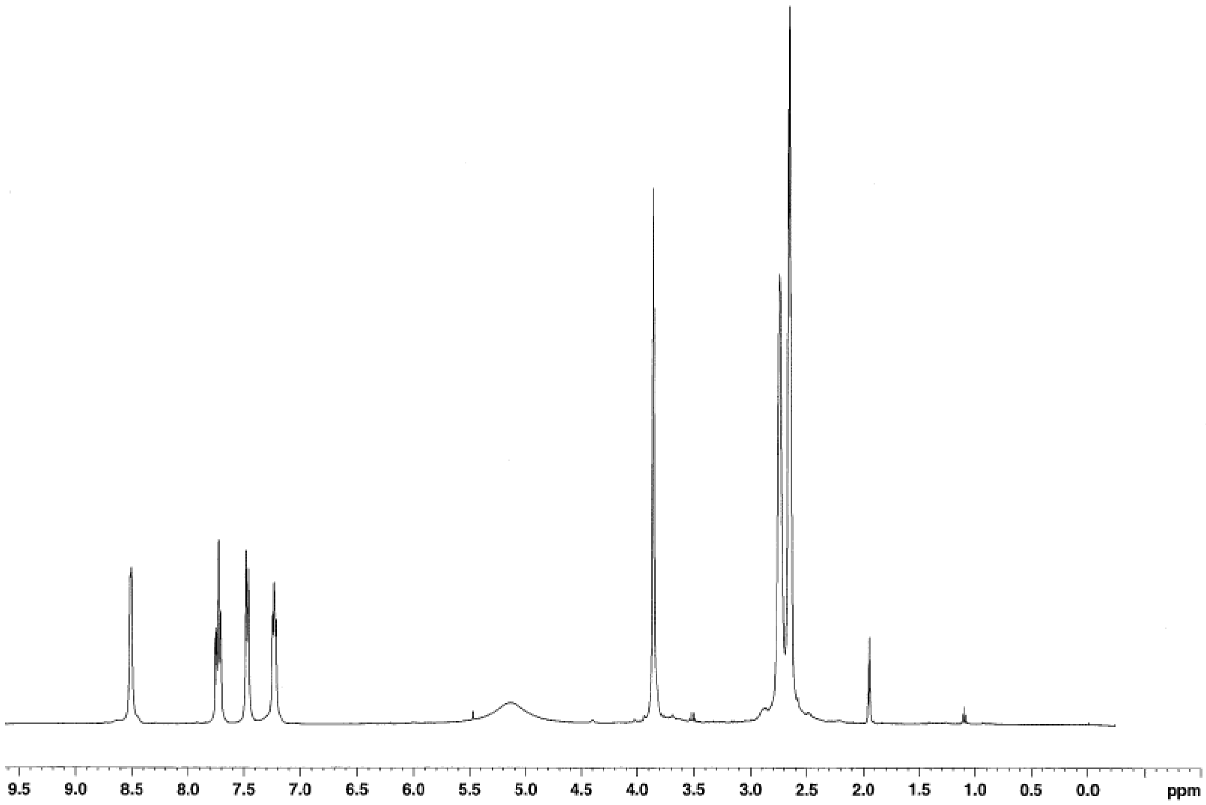


Figure S5. ^{1}H NMR spectrum of Cpy^2 (CD_3CN, 10^{-2} mol dm^{-3}, 400 MHz at 298 K)

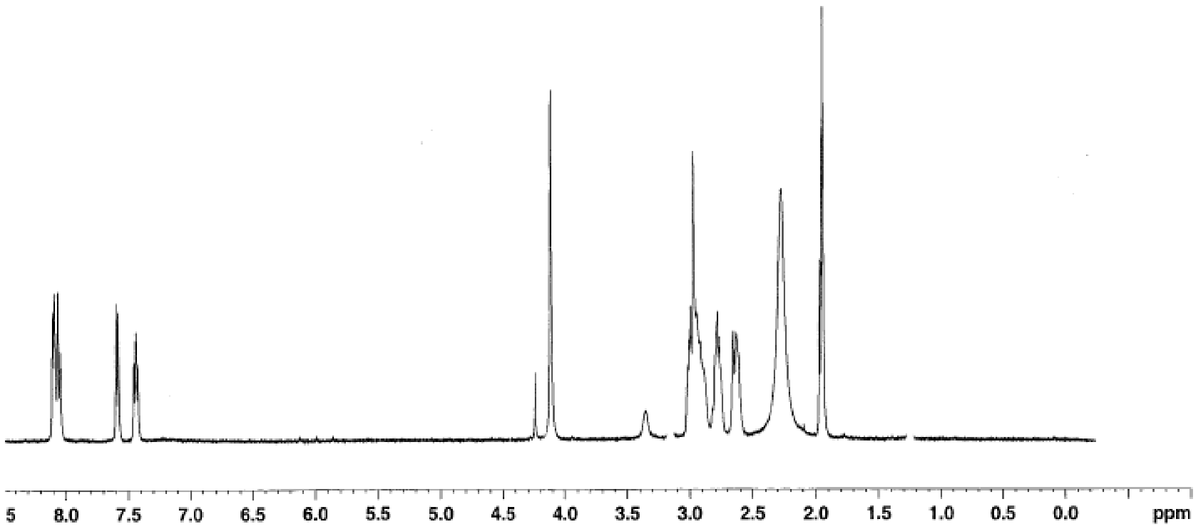


Figure S1.

Figure S6. ^{1}H NMR spectrum of $[Zn(Cpy_2)]^{2+}$ (CD_3CN, 10^{-2} mol dm^{-3}, 400 MHz at 298 K)

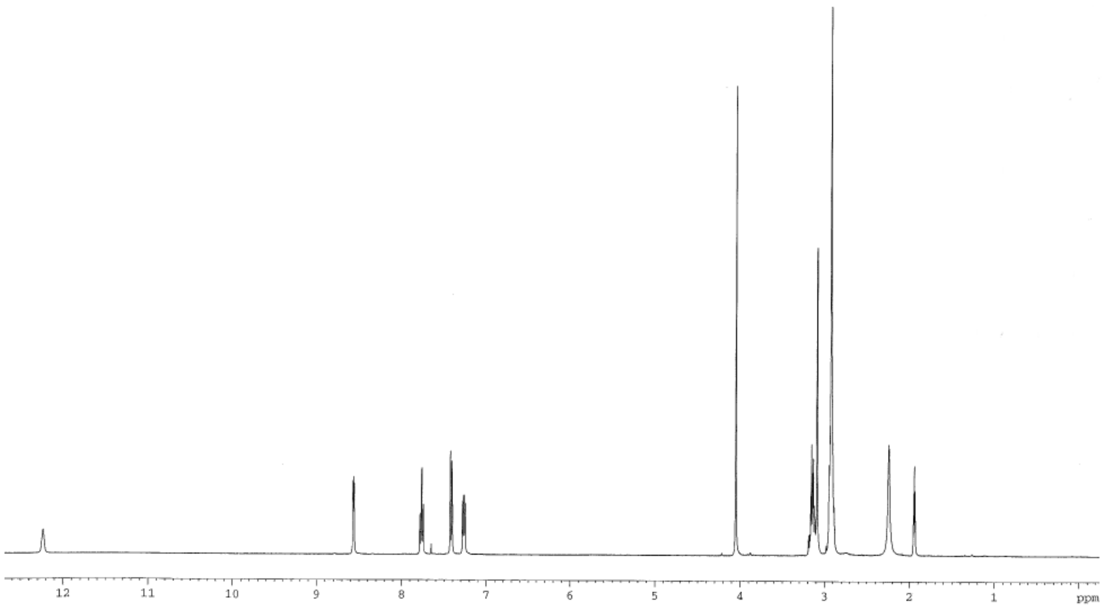


Figure S7. ^{1}H NMR spectrum of CRpy$_2$ (CD$_3$CN, 10^{-2} mol dm^{-3}, 400 MHz at 298 K)

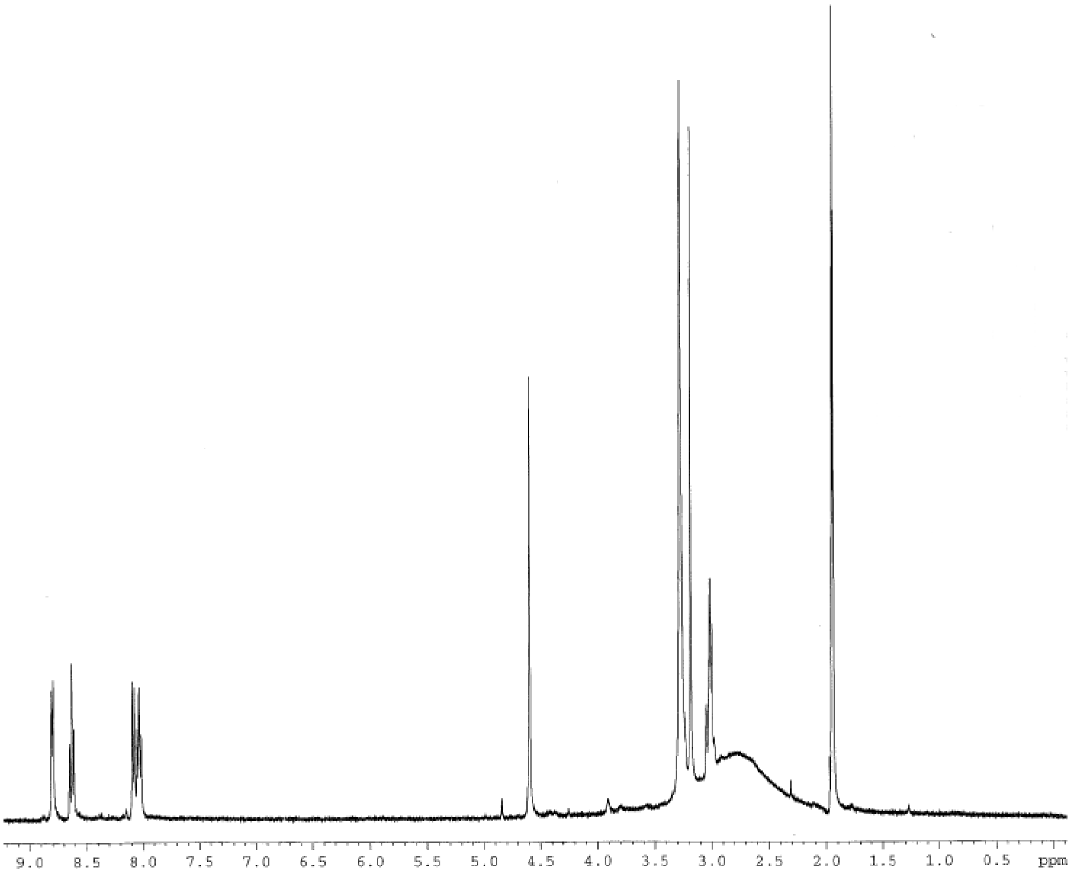


Figure S8. ^{1}H NMR spectrum of [Zn(CRpy$_2$)]$^{2+}$ (CD$_3$CN, 10^{-2} mol dm^{-3}, 400 MHz at 298 K)

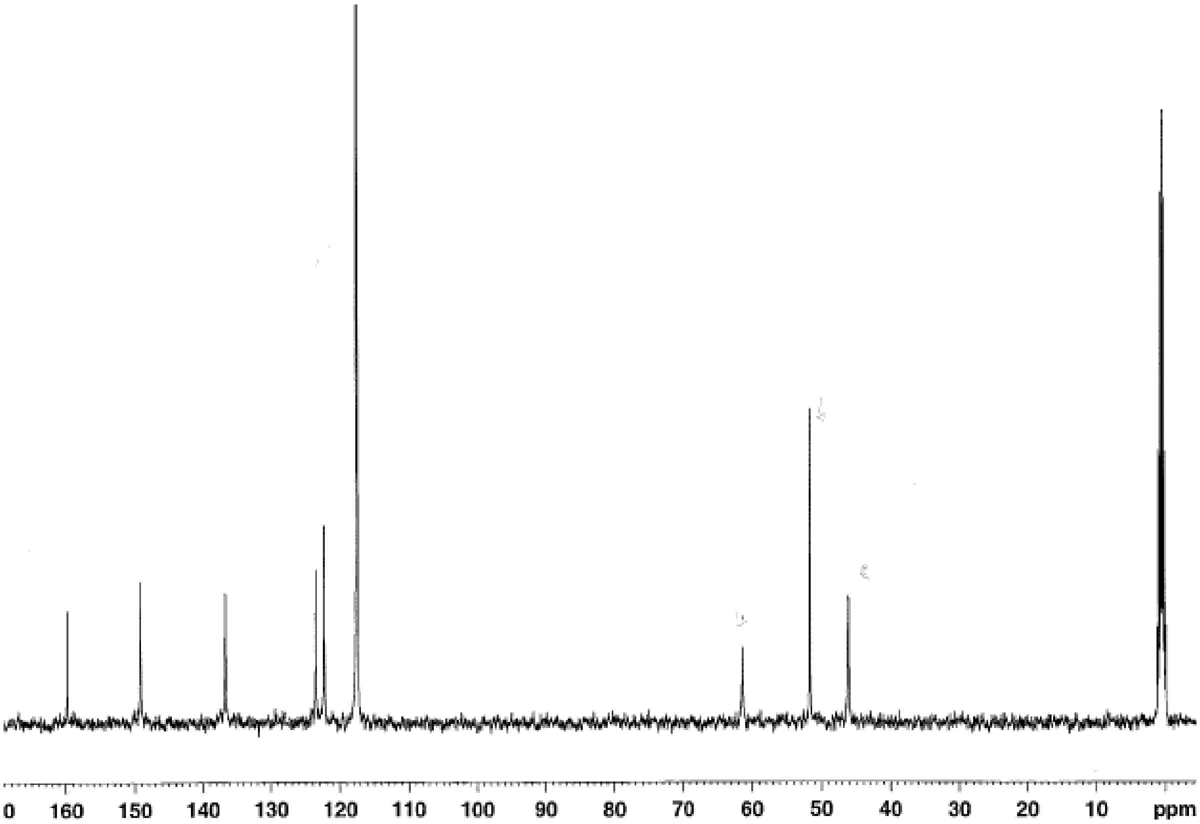


Figure S9. ^{13}C NMR spectrum of Cpy$_2$ (CD$_3$CN, 10^{-2} mol dm^{-3}, 100 MHz at 298 K)

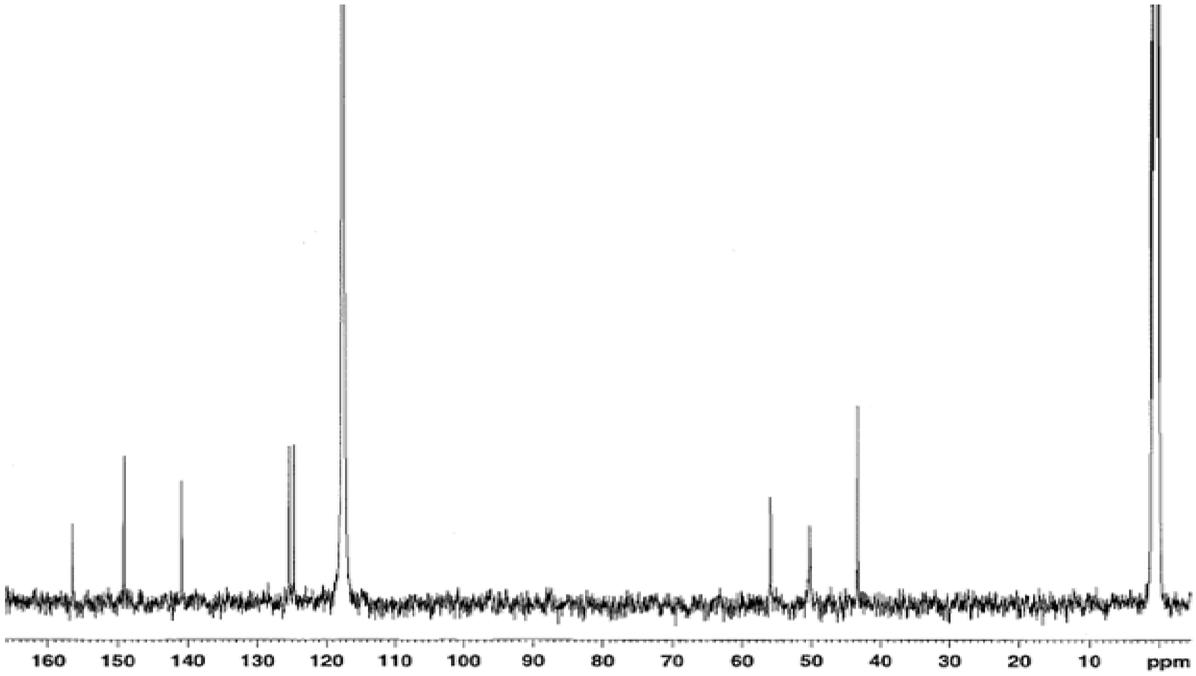


Figure S10. ^{13}C NMR spectrum of [Zn(Cpy$_2$)]$^{2+}$ (CD$_3$CN, 10^{-2} mol dm^{-3}, 100 MHz at 298 K)

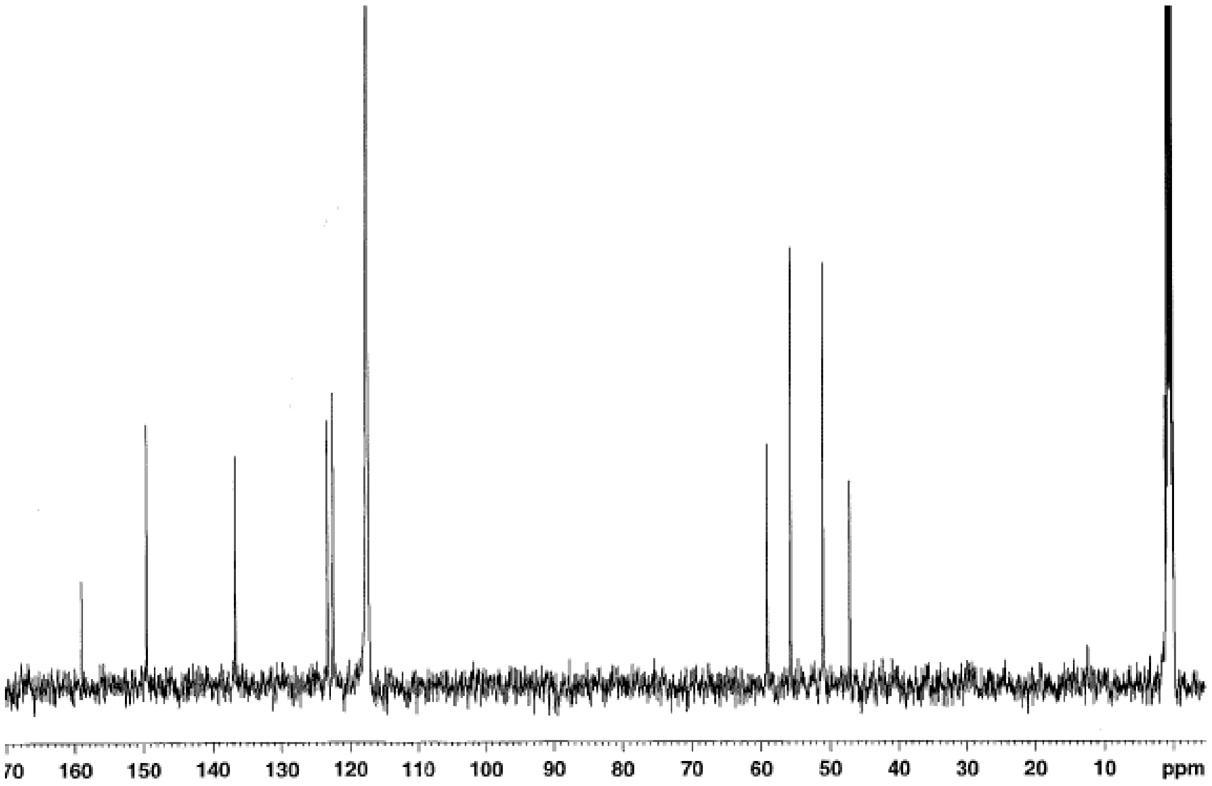


Figure S11. ^{13}C NMR spectrum of CRpy$_2$ (CD$_3$CN, 10^{-2} mol dm^{-3}, 100 MHz at 298 K)

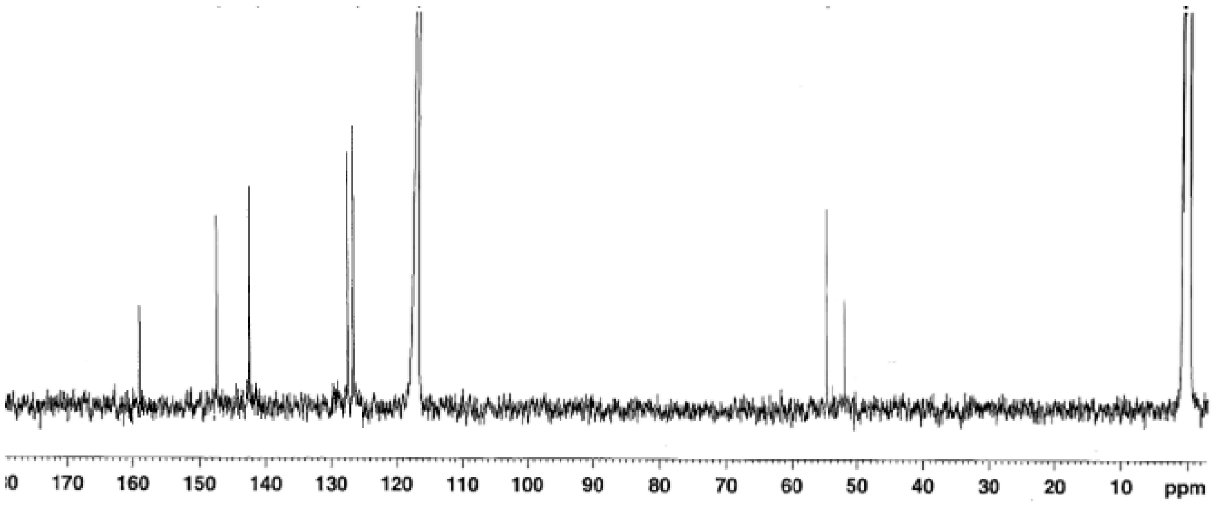


Figure S12. ^{13}C NMR spectrum of [Zn(CRpy$_2$)]$^{2+}$ (CD$_3$CN, 10^{-2} mol dm^{-3}, 100 MHz at 298 K)

Table S5. Overall stability constants ($\beta_{M_m H_h L_l}$) in log units for the metal complexes of Cpy$_2$ and CRpy$_2$ with Co^{2+}, Cu^{2+} and Zn^{2+} metal ions in aqueous solution. T = 298 K and I = 0.1 mol dm^{-3} in NMe$_4$NO$_3$

Metal ion	Equilibrium quotient	Cpy$_2$ [a]	CRpy$_2$ [b]
Co^{2+}	[ML]/[M][L]	17.57(3)	18.18(5)
	[MHL]/[ML][H]	20.96(5)	21.46(5)
	[ML]/[MLOH][H]	8.48(8)	–
Cu^{2+}	[ML]/[M][L]	20.3(1)	19.03(5)
	[MHL]/[ML][H]	23.11(5)	22.86(3)
	[ML]/[MLOH][H]	13.0(1)	–
Zn^{2+}	[ML]/[M][L]	17.51(6)	17.10(4)
	[MHL]/[ML][H]	20.73(8)	–
	[ML]/[MLOH][H]	10.67(8)	–

[a]. Values in brackets are standard deviations in the last significant figure. [b] Values determined by competition with dota.