Electronic Supplementary Information (ESI)

Structure and reactivity of [Ru^{II}(terpy)(N^N)Cl]Cl complexes. Consequences for biological applications

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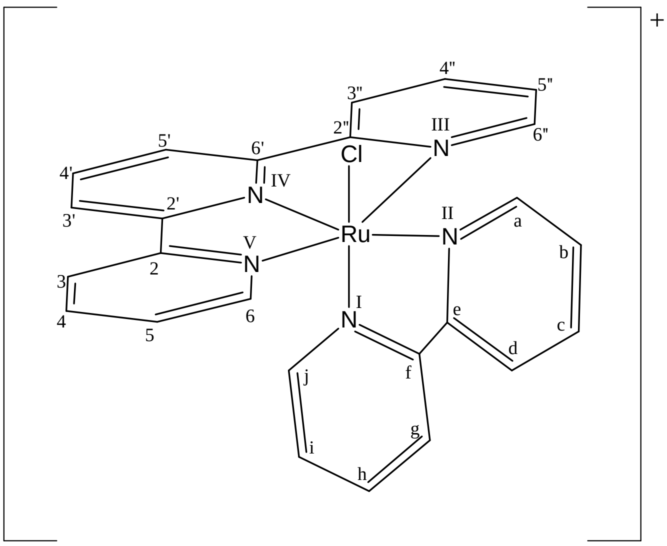
A. Structure of [Ru^{II}(terpy)(bipy)Cl]Cl in solution as determined by NMR spectroscopy



Numbering scheme of terpy and bipy ligands used for NMR characterization

^{1}H NMR (DMSO$_{d-6}$):δ 10.09 (d, 1H, J = 5.6 Hz, Ha), 8.92 (d, 1H, J = 8.2 Hz, Hd), 8.82 (d, 2H, J = 8.1 Hz, H3'/H5'), 8.70 (d, 2H, J = 8.1 Hz, H3/H3"), 8.64 (d, 1H, J = 8.1 Hz, Hg), 8.35 (td, 1H, J_1 = 8.0 Hz, J_2 = 1.4 Hz, Hc), 8.21 (t, 1H, J = 8.0 Hz, H4'), 8.06 (ddd, J_1 = 7.0 Hz, J_2 = 5.6 Hz, J_3 = 1.3 Hz, 1H, Hb), 7.98 (td, 2H, J_1 = 7.6 Hz, J_2 = 1.4 Hz, H4/H4"), 7.77 (td, 1H, J_1 = 7.6 Hz, J_2 = 1.5 Hz, Hh), 7.61 (d, 2H, J = 5.6 Hz, H6/H6"), 7.37 (ddd, J_1 = 7.1 Hz, J_2 = 5.5 Hz, J_3 = 1.3 Hz, 2H, H5/H5"), 7.31 (d, 1H, J = 5.6 Hz, Hj), 7.08 (ddd, J_1 = 7.3 Hz, J_2 = 5.8 Hz, J_3 = 1.4 Hz, 1H, Hi)

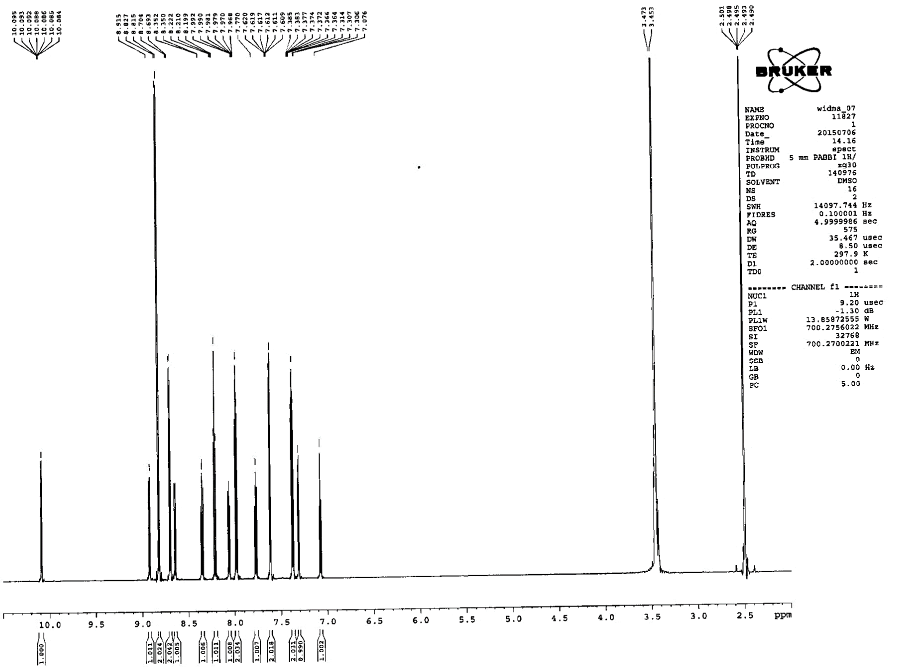
^{13}C NMR (DMSO$_{d-6}$): δ 158.9 (C2/C2"), 158.8 (Cf), 158.0 (C2'/C6'), 156.2 (Ce), 152.4 (Ca), 152.3 (C6/C6"), 152.0 (Cj), 137.5 (C4/C4"), 137.1 (Cc), 136.0 (Ch), 134.3 (C4'), 127.9 (C5/C5"), 127.4 (Cb), 126.9 (Ci), 124.2 (C3/C3"), 124.2 (Cd), 124.0 (Cg), 123.1 (C3'/C5')

^{15}N NMR ($DMSO_{d-6}$): δ −91.9 N(IV), −117.2 N(II), −127.6 N(I), −129.6 N(III)/N(V)

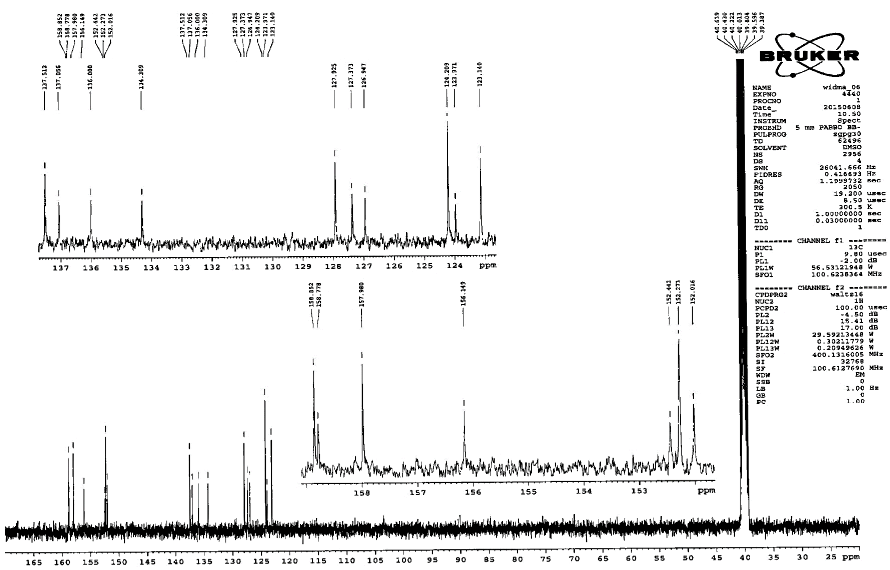
Coordination shift of terpy N signals vs free ligand in dmso:
$\Delta N_{III/V}$ = −56.6 ppm
ΔN_{IV} = −8.3 ppm

NMR spectra

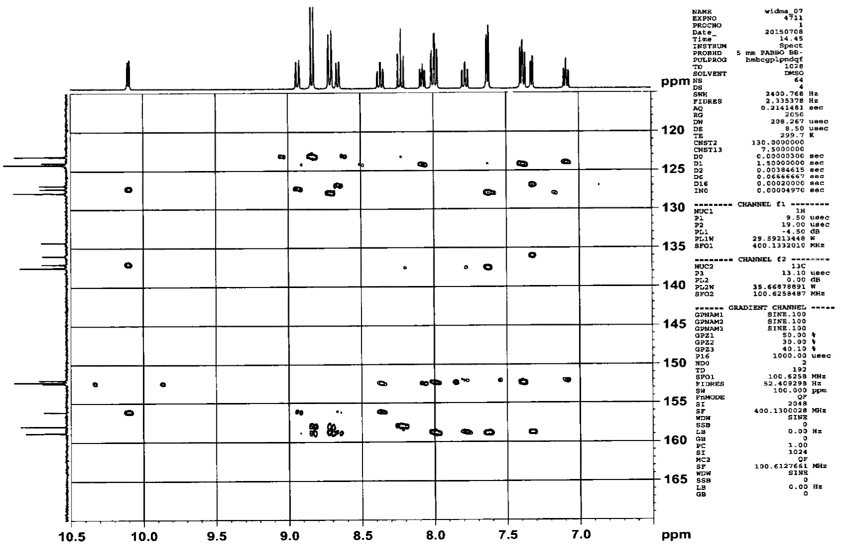
^{1}H NMR



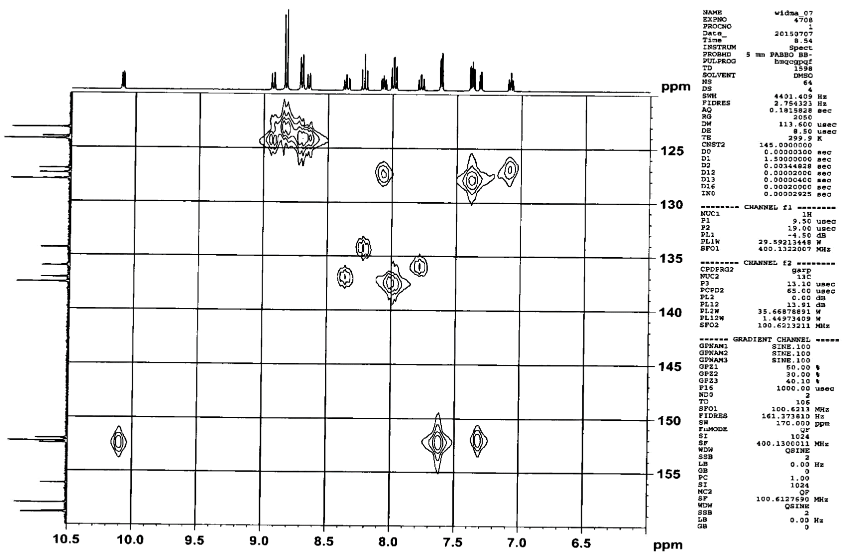
^{13}C NMR



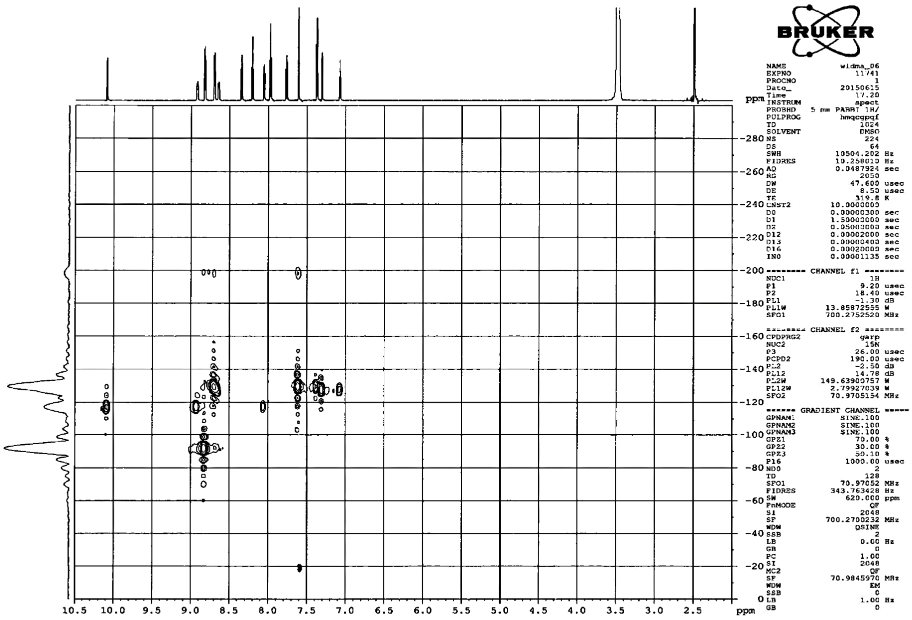
^{1}H-^{13}C HMBC NMR



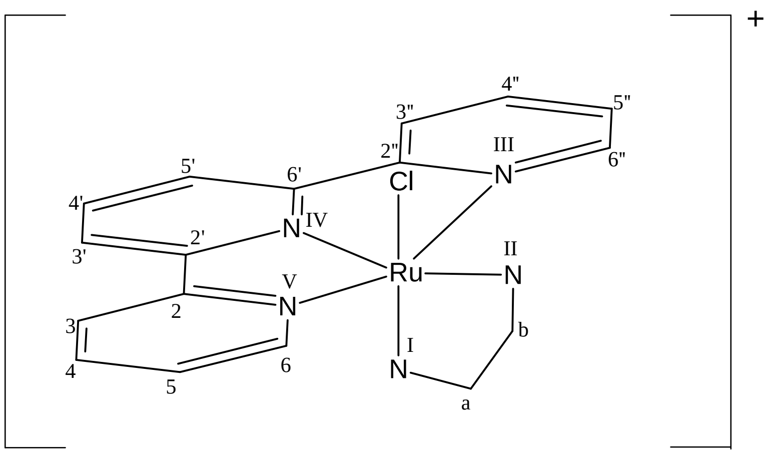
^{1}H-^{13}C HMQC NMR



^{1}H-^{15}N HMQC NMR



B. Structure of [Ru^{II}(terpy)(en)Cl]Cl in solution as determined by NMR spectroscopy



Numbering scheme of terpy and en ligands used for NMR characterization

^{1}H NMR ($DMSO_{d-6}$):δ 9.15 (d, 2H, J = 5.5 Hz, H6/H6’’), 8.60 (d, 2H, J = 8.0 Hz, H3/H3”), 8.56 (d, 2H, J = 8.0 Hz, H3’/H5’), 8.02 (td, 2H, J_1 = 7.7 Hz, J_2 = 1.4 Hz, H4/H4’’), 7.77 (t, 1H, J = 7.9 Hz, H4’), 7.71 (ddd, 2H, J_1 = 7.1 Hz, J_2 = 5.6 Hz, J_3 = 1.3 Hz, H5/H5”), 6.20 (t, br, 2H, J = 5.8 Hz, NH_2(II)), 3.02 (m, 2H, Hb), 2.78 (t, br, J = 5.2 Hz, NH_2(I)), 2.11 (m, 2H, Ha)

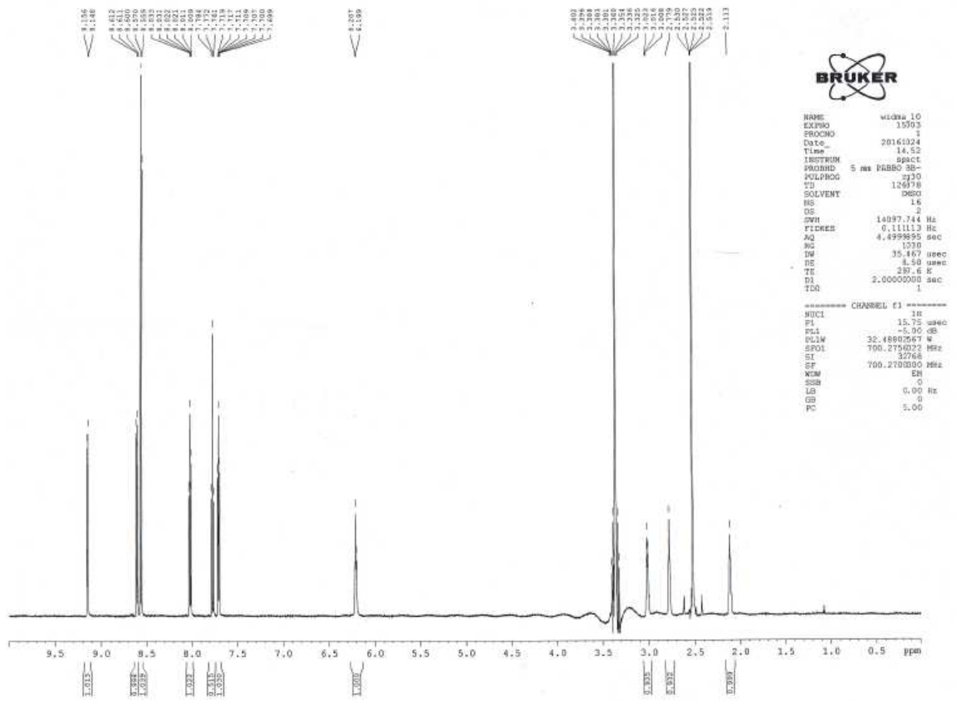
^{13}C NMR ($DMSO_{d-6}$): δ 161.5 (C2/C2”), 161.5 (C2’/C6’), 154.4 (C6/C6”*), 136.5 (C4/C4”), 129.1 (C4’), 127.7 (C5/C5”), 123.7 (C3/C3”), 122.4 (C3’/C5’), 46.5 (Cb), 46.2 (Ca) *split
^{15}N NMR ($DMSO_{d-6}$): δ -78.7 N(IV), -128.5 N(III)/N(V), -375.4 N(II), -399.2 N(I)

Coordination shift of terpy N signals vs free ligand in dmso:
$\Delta N_{III/V}$ = -55.5 ppm

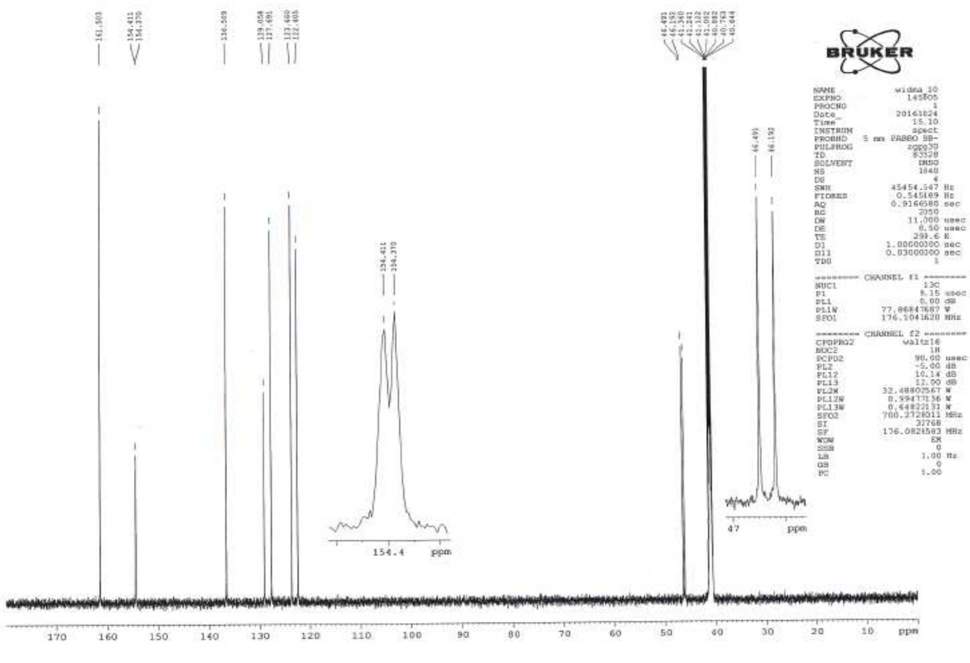
ΔN_{IV} = 4.1 ppm

NMR spectra

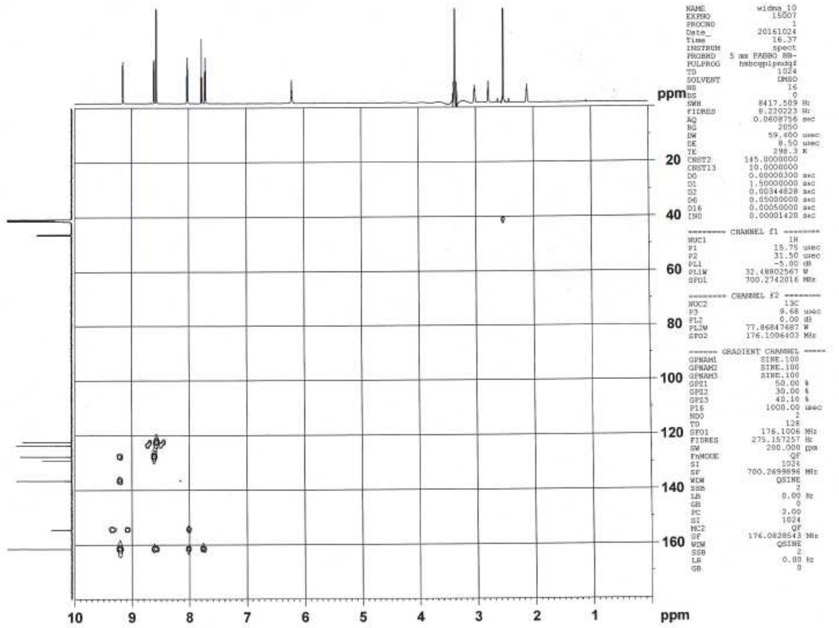
[1]H NMR



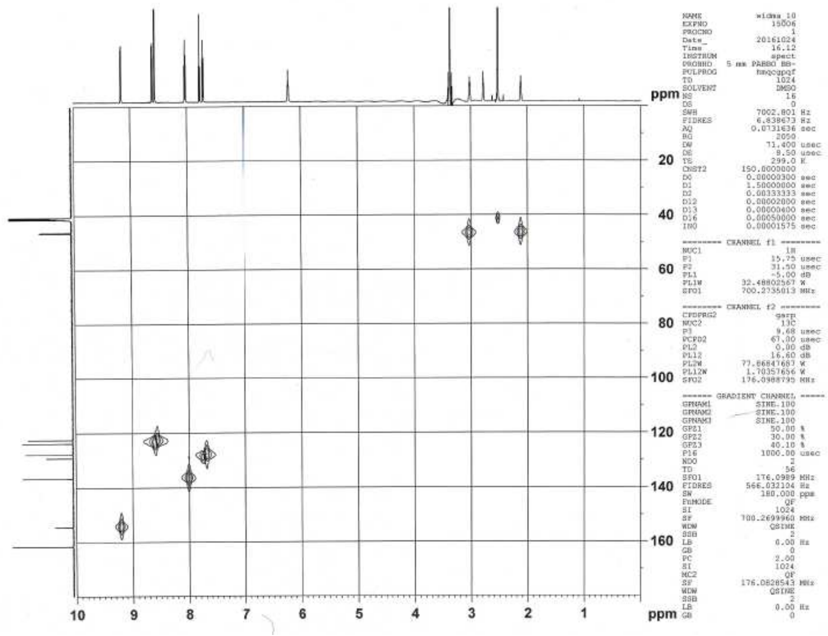
[13]C NMR



^{1}H-^{13}C HMBC NMR



^{1}H-^{13}C HMQC NMR



^{1}H-^{15}N HMQC NMR

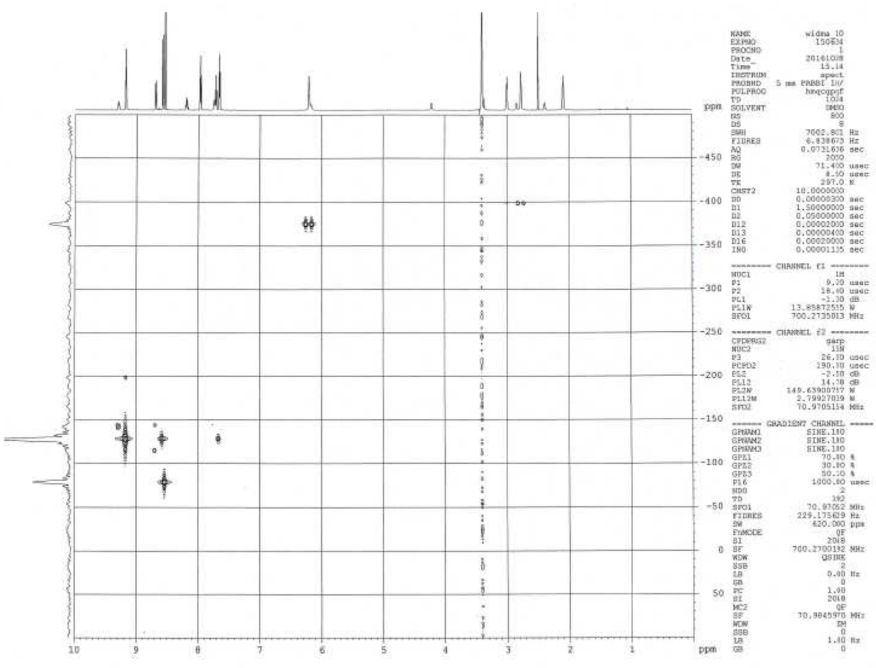


Table S1. Dependence of k_{obs} on temperature for the reaction of $[Ru(terpy)(bipy)(H_2O)]^{2+}$ with chloride[a]

T, °C	$10^3 k_{obs}$, s^{-1}	$10^3 k_1$, M^{-1} s^{-1}	$\Delta H^{\neq}$, kJ mol^{-1}	$\Delta S^{\neq}$, J K^{-1} mol^{-1}
20.2	0.53 ± 0.03	0.211	78 ± 2	–46 ± 5
29.6	1.66 ± 0.03	0.666		
39.4	4.94 ± 0.02	1.97		
49.3	12.5 ± 0.1	5.01		

[a] Experimental conditions: [Ru(II)] = 7.1 x 10^{-5} M, [Cl^-] = 2.5 M, I = 2.5 M (NaCl).

Table S2. Dependence of k_{obs} on temperature for the reaction of $[Ru(terpy)(bipy)(H_2O)]^{2+}$ with thiourea[a]

T, °C	$10^3 k_{obs}$, s^{-1}	$10^3 k_2$, M^{-1} s^{-1}	$\Delta H^{\neq}$, kJ mol^{-1}	$\Delta S^{\neq}$, J K mol^{-1}
26.4	0.18 ± 0.02	0.60	82.9 ± 0.8	–29 ± 2
30.9	0.35 ± 0.03	1.16		
36.3	0.62 ± 0.04	2.08		
43.6	1.33 ± 0.01	4.42		
51.8	3.01 ± 0.02	10.0		

[a] Experimental conditions: [Ru(II)] = 5.9 x 10^{-5} M, [TU] = 0.3 M, I = 0.1 M ($NaNO_3$).

Table S3. Dependence of k_{obs} on temperature for the reaction of $[Ru(terpy)(en)(H_2O)]^{2+}$ with thiourea[a]

T, °C	$10^3 k_{obs}$, s^{-1}	$10^3 k_2$, M^{-1} s^{-1}	$\Delta H^{\neq}$, kJ mol^{-1}	$\Delta S^{\neq}$, J K^{-1} mol^{-1}
10.8	1.53 ± 0.02	7.64	65 ± 2	–55 ± 6
16.0	2.76 ± 0.01	13.8		
20.5	4.29 ± 0.05	21.4		
25.5	7.53 ± 0.01	37.7		
30.5	11.2 ± 0.2	56.2		
34.8	16.0 ± 0.2	80.1		

[a] Experimental conditions: [Ru(II)] = 1.2 x 10^{-4} M, [TU] = 0.2 M, I = 0.1 M ($NaNO_3$).

Table S4. Dependence of k_{obs} on temperature for the reaction of $[Ru(terpy)(en)(H_2O)]^{2+}$ with cyanide[a]

T, °C	$10^4 k_{obs}$, s^{-1}	$10^3 k_3$, $M^{-1} s^{-1}$	$\Delta H^{\neq}$, kJ mol^{-1}	$\Delta S^{\neq}$, J K^{-1} mol^{-1}
11.5	2.28 ± 0.03	4.55	83 ± 2	+2 ± 6
17.7	4.50 ± 0.01	9.00		
22.4	7.90 ± 0.01	15.8		
27.7	15.4 ± 0.2	30.7		
31.3	22.4 ± 0.5	44.7		

[a] Experimental conditions: [Ru(II)] = 1.9 x 10^{-4} M, $[CN^-]$ = 0.05 M, pH = 10.5, I = 1 M ($NaNO_3$).

Table S5. Summary of computational data for water exchange reactions on complexes of the type [Ru(terpy)(N^N)(OH_2)]$^{2+}$. All ZPE corrections were derived from the B3LYP/def2svp-calculations; GS: ground state, TS: transition state

[Ru(terpy)(bipy)(H_2O)]$^{2+}$ + H_2O	E_{tot} (GS) [a.u.]	ZPE (TS) [kcal mol^{-1}]	E_{tot} (TS) [a.u.]	ZPE (TS) [kcal mol^{-1}]	ΔE_{tot} [kcal mol^{-1}]	ΔZPE [kcal mol^{-1}]	ΔE [kcal mol^{-1}]
B3LYP/def2svp	-1484.34842	278.14	-1484.31095	277.08	23.51	-1.06	22.46
B3LYP/def2tzvp//B3LYP/def2svp	-1485.87659	278.14	-1485.84246	277.08	21.42	-1.06	20.36
B3LYP(CPCM)/def2tzvp//B3LYP/def2svp	-1486.07068	278.14	-1486.03999	277.08	19.26	-1.06	18.20
ωB97XD/def2tzvp//B3LYP/def2svp	-1485.39353	278.14	-1485.35949	277.08	21.36	-1.06	20.30
ωB97XD(CPCM)/def2tzvp//B3LYP/def2svp	-1485.58665	278.14	-1485.55585	277.08	19.33	-1.06	18.27

[Ru(terpy)(en)(H_2O)]$^{2+}$ + H_2O (H_2O···H_2NR)	E_{tot} (GS) [a.u.]	ZPE (TS) [kcal mol^{-1}]	E_{tot} (TS) [a.u.]	ZPE (TS) [kcal mol^{-1}]	ΔE_{tot} [kcal mol^{-1}]	ΔZPE [kcal mol^{-1}]	ΔE [kcal mol^{-1}]
B3LYP/def2svp	-1179.67674	249.64	-1179.64548	248.92	19.61	-0.72	18.89
B3LYP/def2tzvp//B3LYP/def2svp	-1180.88637	249.64	-1180.85924	248.92	17.03	-0.72	16.31
B3LYP(CPCM)/def2tzvp//B3LYP/def2svp	-1181.09945	249.64	-1181.07502	248.92	15.32	-0.72	14.60
ωB97XD/def2tzvp//B3LYP/def2svp	-1180.52312	249.64	-1180.49519	248.92	17.53	-0.72	16.81
ωB97XD(CPCM)/def2tzvp//B3LYP/def2svp	-1180.73480	249.64	-1180.70959	248.92	15.82	-0.72	15.10

[Ru(terpy)(en)(H_2O)]$^{2+}$ + H_2O (H_2O···H_2O)	E_{tot} (GS) [a.u.]	ZPE (TS) [kcal mol^{-1}]	E_{tot} (TS) [a.u.]	ZPE (TS) [kcal mol^{-1}]	ΔE_{tot} [kcal mol^{-1}]	ΔZPE [kcal mol^{-1}]	ΔE [kcal mol^{-1}]
B3LYP/def2svp	-1179.68161	249.84	-1179.64548	248.92	22.67	-0.92	21.75
B3LYP/def2tzvp//B3LYP/def2svp	-1180.89147	249.84	-1180.85924	248.92	20.23	-0.92	19.30
B3LYP(CPCM)/def2tzvp//B3LYP/def2svp	-1181.10494	249.84	-1181.07502	248.92	18.77	-0.92	17.85
ωB97XD/def2tzvp//B3LYP/def2svp	-1180.52738	249.84	-1180.49519	248.92	20.20	-0.92	19.28
ωB97XD(CPCM)/def2tzvp//B3LYP/def2svp	-1180.73959	249.84	-1180.70959	248.92	18.83	-0.92	17.91

$[Ru(terpy)(enMe_2)(H_2O)]^{2+} + H_2O$	E_{tot} (GS) [a.u.]	ZPE (TS) [kcal mol^{-1}]	E_{tot} (TS) [a.u.]	ZPE (TS) [kcal mol^{-1}]	ΔE_{tot} [kcal mol^{-1}]	ΔZPE [kcal mol^{-1}]	ΔE [kcal mol^{-1}]
B3LYP/def2svp	-1258.22194	285.10	-1258.18508	284.40	23.13	-0.70	22.43
B3LYP/def2tzvp//B3LYP/def2svp	-1259.51685	285.10	-1259.48259	284.40	21.50	-0.70	20.80
B3LYP(CPCM)/def2tzvp//B3LYP/def2svp	-1259.72423	285.10	-1259.69428	284.40	18.79	-0.70	18.09
ωB97XD/def2tzvp//B3LYP/def2svp	-1259.13554	285.10	-1259.10210	284.40	20.98	-0.70	20.28
ωB97XD(CPCM)/def2tzvp//B3LYP/def2svp	-1259.34172	285.10	-1259.31246	284.40	18.36	-0.70	17.66

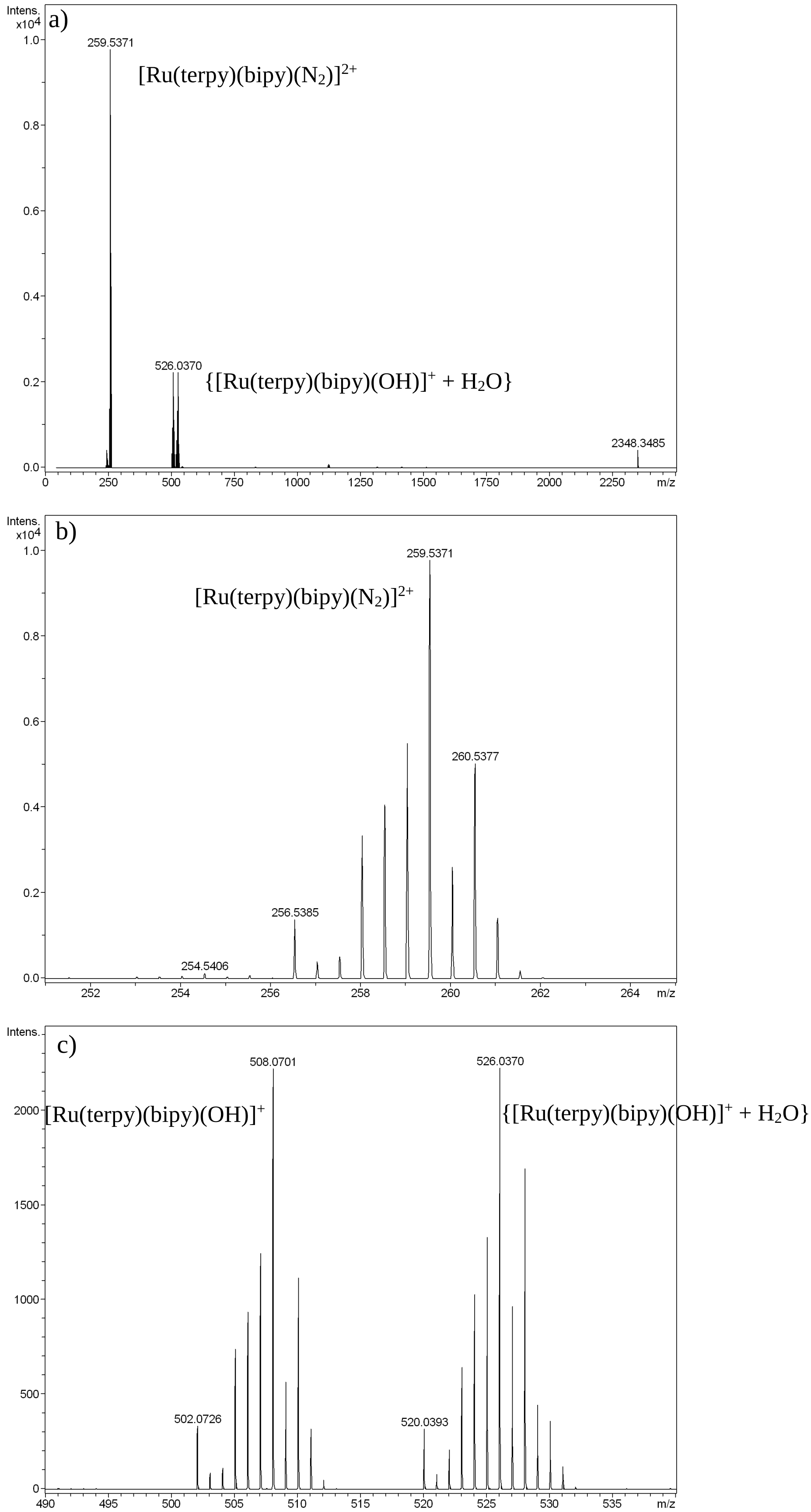


Figure S1. ESI-MS spectra of $[Ru(terpy)(bipy)(H_2O)]^{2+}$.

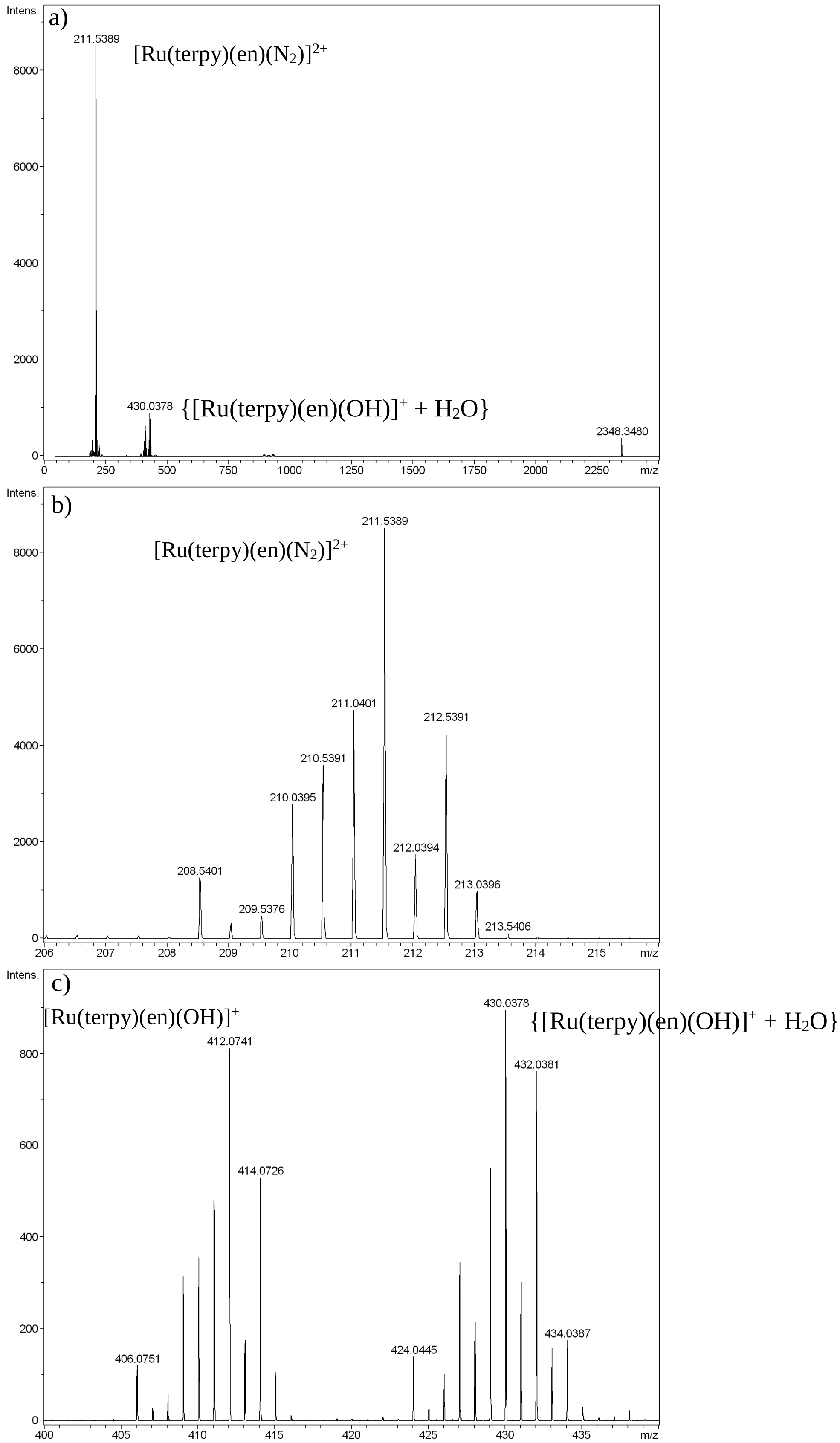


Figure S2. ESI-MS spectra of $[Ru(terpy)(en)(H_2O)]^{2+}$.

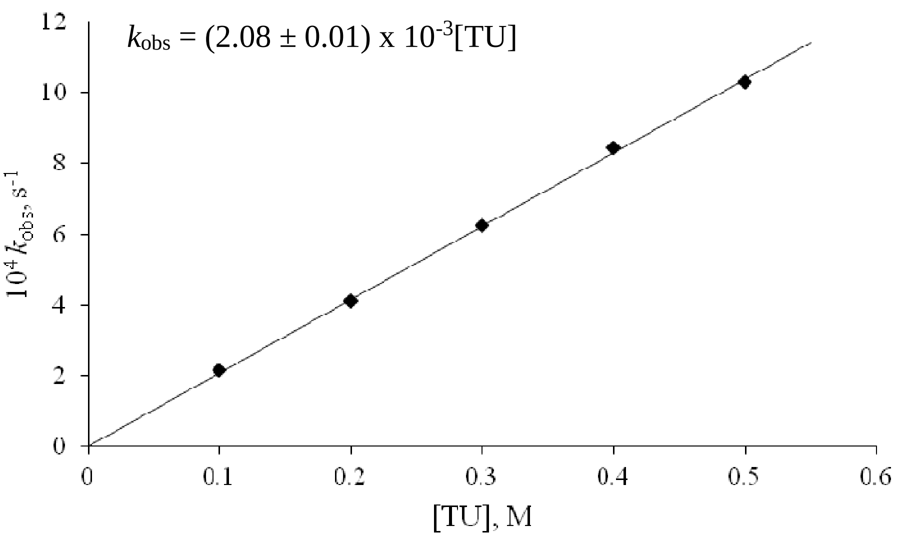


Figure S3. Plot of k_{obs} versus thiourea concentration for the reaction of $[Ru^{II}(terpy)(bipy)(H_2O)]^{2+}$ with thiourea. Experimental conditions: [Ru(II)] = 5.9 x 10^{-5} M, I = 0.1 M ($NaNO_3$), T = 36.3 °C.

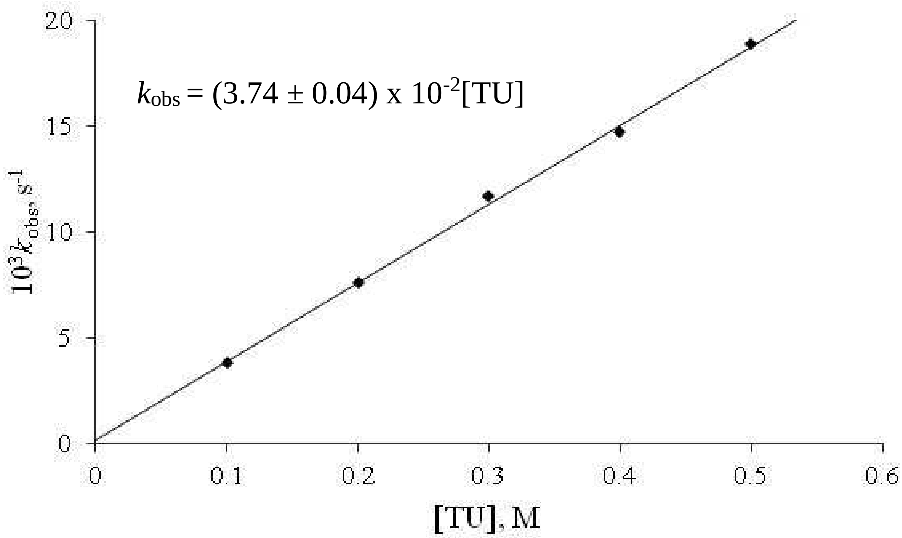


Figure S4. Plot of k_{obs} versus thiourea concentration for the reaction of $[Ru^{II}(terpy)(en)(H_2O)]^{2+}$ with thiourea. Experimental conditions: [Ru(II)] = 1.2 x 10^{-4} M, I = 0.1 M ($NaNO_3$), T = 25 °C.

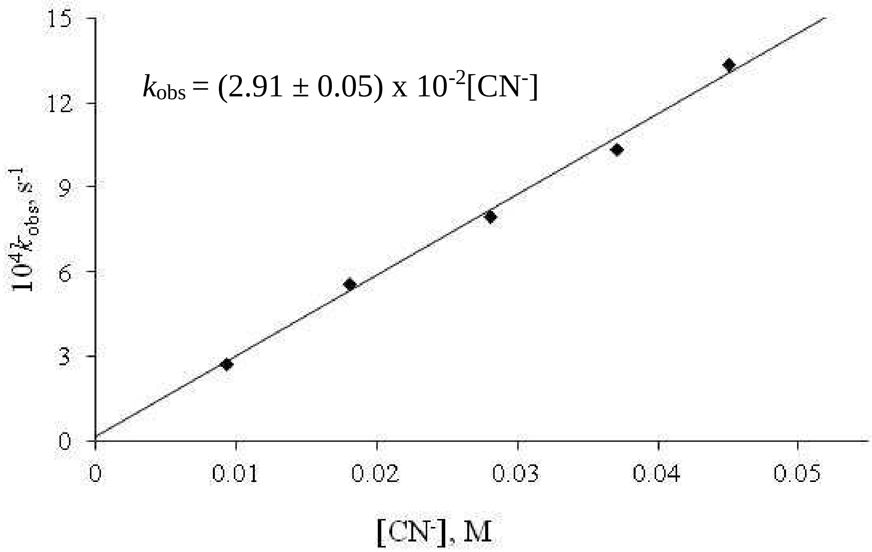


Figure S5. Plot of k_{obs} versus cyanide concentration for the reaction of $[Ru^{II}(terpy)(en)(H_2O)]^{2+}$ with cyanide. Experimental conditions: [Ru(II)] = 1.9 x 10^{-4} M, pH = 10.25, I = 1 M ($NaNO_3$), T = 25 °C.

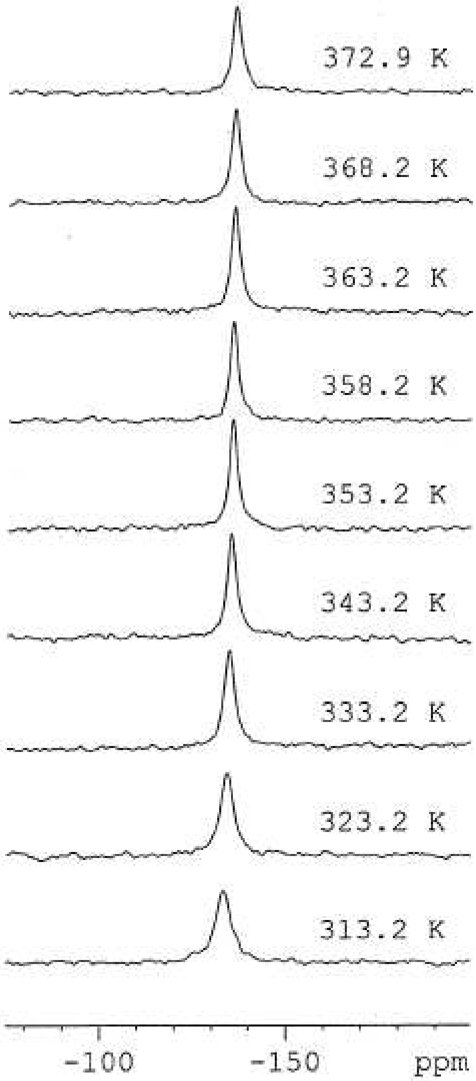


Figure S6. 54.24 MHz ^{17}O-NMR spectra of 0.03 M $[Ru^{II}(terpy)(en)(H_2O)]^{2+}$ in aqueous solution containing 30% (v/v) of 10%-enriched $^{17}OH_2$ and 0.1 M $MnSO_4$. The spectra were recorded in the temperature range from 313.2 to 372.9 K and are the result of 30k (30720) scans using a relaxation delay of 0.15 s, an acquisition time of 0.1 s and a pulse width of 16.7 μs in the quadratic detection mode.