Supplementary data for the article:

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SUPPLEMENTARY INFORMATION

Comparative solution and structural studies of half-sandwich rhodium and ruthenium complexes bearing curcumin and acetylacetone

János P. Mészáros, Jelena M. Poljarevic, G. Tamás Gál, Nóra V. May, Gabriella Spengler, and Éva A. Enyedy*

Synthesis of the precursor [Ru(η^6-tol)(μ^2-Cl)Cl]$_2$

[Ru(η^6-tol)(μ^2-Cl)Cl]$_2$ was prepared according the literature procedure used for the analogous [Ru(η^6-benzene)(μ^2-Cl)Cl]$_2$ [1] by adding 5 mL of 1-methyl-1,4-cyclohexadiene to a solution of 0.5 g $RuCl_3 \times 3H_2O$ (1.9 mmol) in 40 mL of absolute ethanol. This mixture was refluxed for 8 h. The reddish brown precipitate formed during the synthesis was filtered off, washed with diethyl ether and left to dry in exsiccator. Yield: 85%, 0.450 g; ^{1}H NMR (500.26 MHz, DMSO-d_6, δ, ppm): 2.12 (3H, s, CH_3), 5.68 (3H, m, C2, C4, C6 toluene), 5.97 (2H, m, C3, C5 toluene); ^{13}C NMR (125.79 MHz, DMSO-d_6, δ, ppm) 18.73 (CH_3), 82.22 (C4 toluene), 84.83 (C5, C3 toluene), 89.28 (C6, C2 toluene), 105.82 (C1 toluene); HRMS (m/z): found: 279.8999 (calculated for $RuC_7H_8Cl_2O$ [Ru(η^6-tol)Cl_2O]$^+$: 279.8996).

References

[1] R.A. Zelonka, M.C. Baird, Can. J. Chem. 50 (1972) 3063–3072.

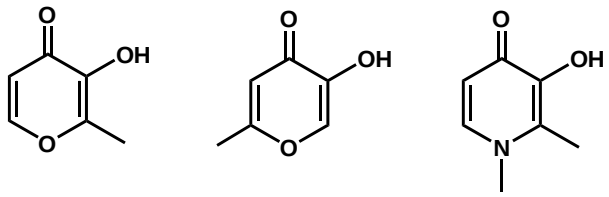


Chart S1. Chemical structures of maltol, allomaltol and deferiprone.

Table S1. Crystal data and structure refinement for [Ru(η^6-tol)(acac)Cl] (**1**) and [Rh(η^5-C_5Me_5)(H_2curc)Cl] × 2MeOH (**2**). [a]

	[Ru(η^6-tol)(acac)Cl] (**1**)	[Rh(η^5-C_5Me_5)(H_2curc)Cl] × 2MeOH (**2**)
CCDC number	1882689	1882690
Empirical formula	$C_{12}H_{15}ClO_2Ru$	$C_{33}H_{42}ClO_8Rh$ × 2MeOH
Formula weight	327.76	705.02
Temperature	103(2)	103(2)
Radiation and	Mo-K_α, λ =0.71075Å	Cu-K_α, λ =1.54178
Crystal system	monoclinic	othorombic
Space group	$P2_1/c$	*Pbcn*
Unit cell dimensions	*a* =8.5579(9)Å	*a* =17.3703(3)Å
	b =9.9459(12)Å	*b* =23.7039(4)Å
	c =14.7303(15)Å	*c* =15.7300(3)Å
	β = 98.009(7)°	β = 90°
Volume	1241.6(2)Å^3	6476.7(2) Å^3
Z	4	8
Density (calculated)	1.753 g/cm^3	1.446 g/cm^3
Absorption coefficient,	1.460 mm^{-1}	5.431 mm^{-1}
F(000)	656	2928
Crystal colour/	yellow / prism	red / prism
Crystal size	0.347 x 0.080 x 0.073 mm	0.50 x 0.30 x 0.20 mm
Absorption correction	numerical	multi-scan
Max. and min.	0.924 and 0.981	0.893 and 0.931
θ-range for data	3.158 ≤ θ ≤ 27.450°	3.154° ≤ θ ≤ 68.242°
Index ranges	-10 ≤ *h* ≤ 11;-12≤ *k* ≤12;-19 ≤ *l*	-20 ≤ *h* ≤ 20;-27≤ *k* ≤28;-16 ≤ *l* ≤ 18
Reflections collected	10540	83894
Completeness to 2θ	0.998	0.999
Independent reflections	2823 [*R*(int) =0.0883]	5928 [*R*(int) =0.0842]
Reflections *I*>2σ(*I*)	1972	5766
Refinement method	full-matrix least-squares on F^2	
Data / restraints /	2823 /0 /148	5928 / 0 / 397
Goodness-of-fit on F^2 [b]	1.063	1.268
Final *R* indices	*R*1 =0.0668, *wR*2 =0.1039	*R*1 =0.0426, *wR*2 =0.0923
R indices (all data) [c]	*R*1 =0.1100, *wR*2 =0.1159	*R*1 =0.0444, *wR*2 =0.0930
Max. and mean	0.000; 0.000	0.001; 0.000
Largest diff. peak and	1.351;-1.423 e.Å^{-3}	0.907;-740 e.Å^{-3}

[a] Uncertainties (SD) of the last digits are shown in parentheses

[b] GOF = $\{\Sigma[w(F_o^2 - F_c^2)^2]/(n-p)\}^{1/2}$, where *n* is the number of reflections and *p* is the total number of parameters refined.

[c] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$

Table S2. Intramolecular interactions in crystal [Ru(η^6-tol)(acac)Cl] (**1**).

D-H...A	symmetry operation	D-H (Å)	H...A (Å)	D...A (Å)	D-H...A (^{o})
C2-H2…O2	1-x,-1/2+y,1/2-z	0.95	2.53	3.278(8)	136
C4-H4…O1	1-x,1/2+y,1/2-z	0.95	2.43	3.375(10)	171
C5-H5…Cl1	1-x,1/2+y,1/2-z	0.95	2.81	3.598(7)	140
C6-H6…O2	1-x,1-y,-z	0.95	2.47	3.365(8)	156

Table S3. Intermolecular interactions in crystal [Rh(η^5-C_5Me_5)(H_2curc)Cl] × 2MeOH (**2**).

D-H…A	symmetry operation	D…H (Å)	H…A (Å)	D…A (Å)	D-H…A (^{o})
O3-H3…O8	1/2-x,1/2+y,z	0.82	1.81	2.631(4)	173
O5-H5…Cl1	-1/2+x,-1/2+y	0.82	2.24	3.017(2)	157
O8-H8…Cl1	-x,1-y,-z	0.82	2.42	3.160(3)	151
O9-H9…O3	1/2-x,1/2-y	0.82	2.05	2.866(1)	170
C22-H22…O9	x,-y,1/2+z	0.93	2.53	3.409(4)	158
C31-H31B…O5	-x,y,1/2-z	0.96	2.48	3.415(5)	165
C9-H9C…Cg(D)	-x,1-y,-z	0.96	2.95	3.722(4)	138

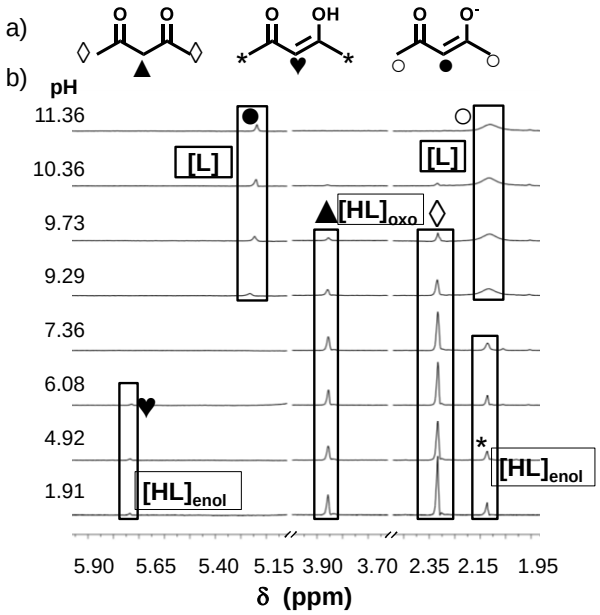


Figure S1. a) Chemical structures of oxo-, enol- and enolate forms of acetylacetone with peak assignation. b) ^{1}H NMR spectra of acetylacetone at pH = 1.9-11.4. {*c*(acac) = 2 mM; solvent: 90% H_2O / 10% D_2O; *T* = 25.0 °C; *I* = 0.2 M (KCl)}

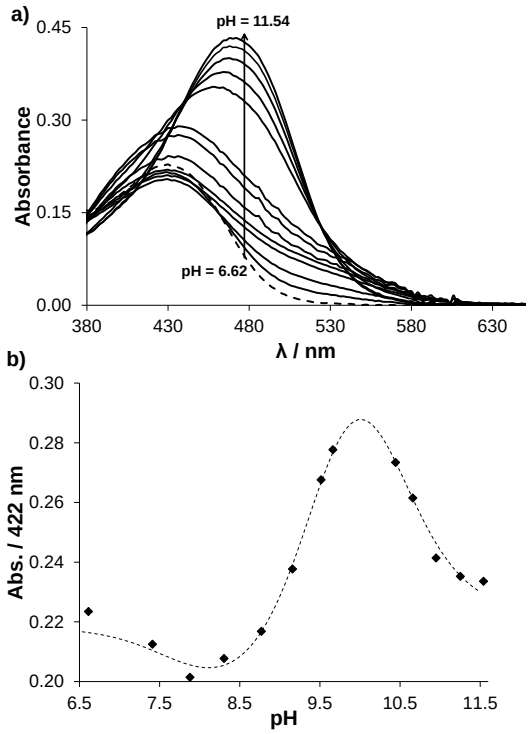


Figure S2. a) UV-Vis absorption spectra of curcumin recorded at pH = 6.6-11.5 using individual samples kept in dark. b) Measured (♦) and fitted values (dashed line) of absorbance values at 422 nm. {*c*(curcumin) = 5 μM; solvent: 95% H_2O / 5% MeOH; ℓ = 2 cm; *T* = 25.0 °C; *I* = 0.2 M (KCl)}

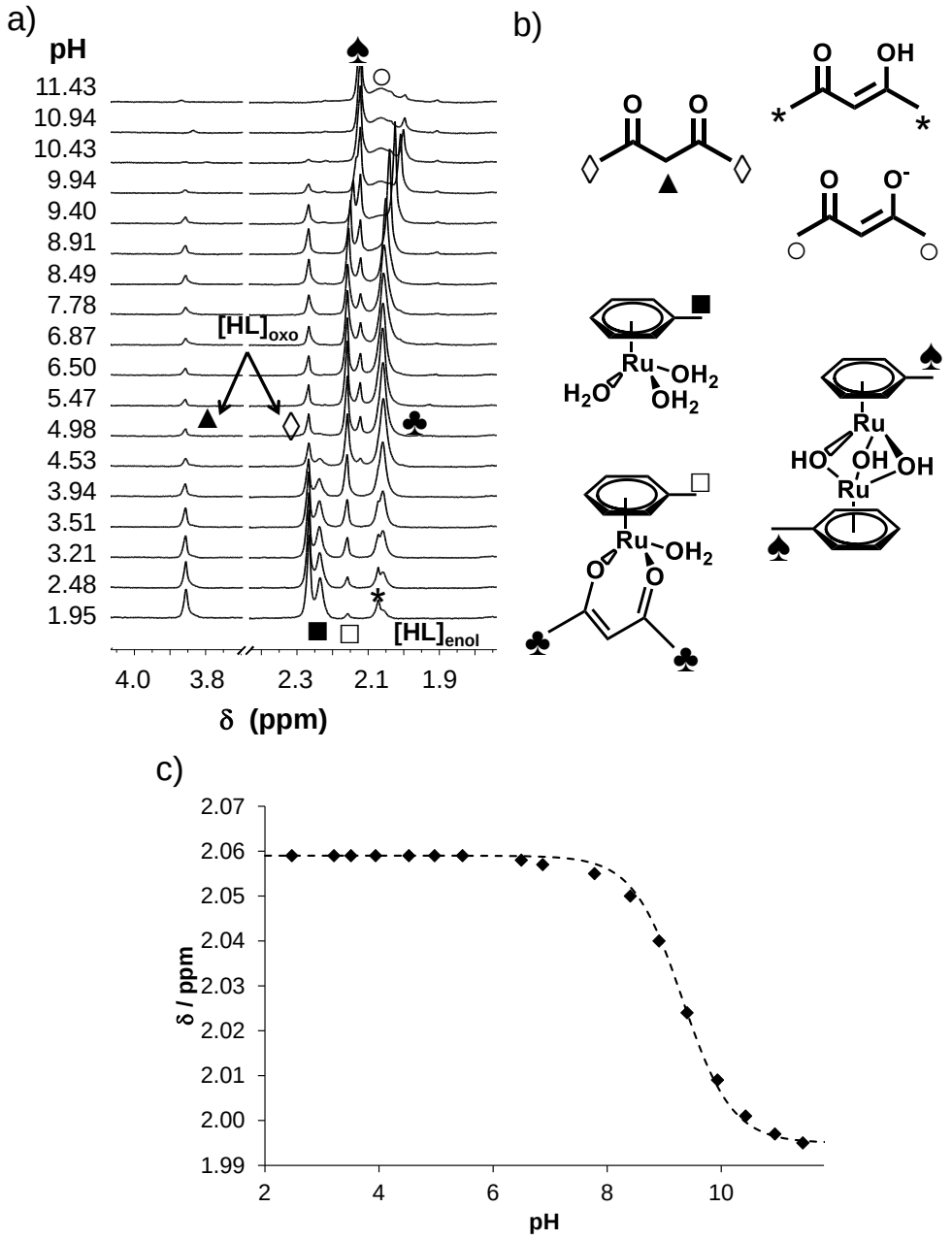


Figure S3. a) ^{1}H NMR spectra of $[Ru(\eta^6\text{-tol})(H_2O)_3]^{2+}$– acac system recorded at pH = 1.9-11.4. b) Chemical structures of compounds present in the $[Ru(\eta^6\text{-tol})(H_2O)_3]^{2+}$– acac system. b) Peak assignation is indicated on the structures. c) Measured (♦) and fitted (dashed line) chemical shift values of the methyl groups of coordinated acac in the function of pH. {*c*(acac) = *c*($[Ru(\eta^6\text{-tol})(H_2O)_3]^{2+}$) = 2 mM; solvent: 90% H_2O / 10% D_2O; *T* = 25.0 °C; *I* = 0.2 M (KCl)}

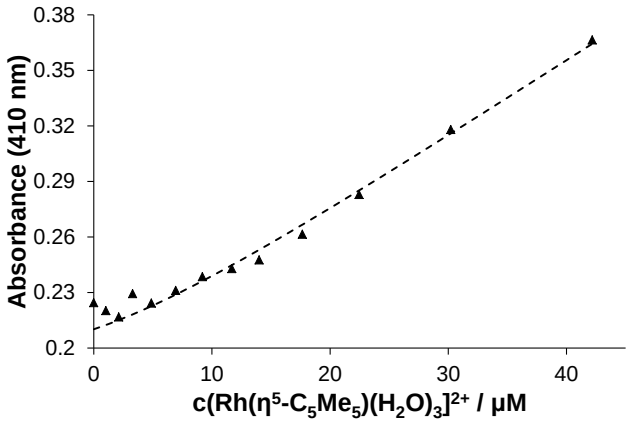


Figure S4. Measured (▲) and fitted (dashed line) absorbance values at 410 nm in the function of $[Rh(\eta^5\text{-}C_5Me_5)(H_2O)_3]^{2+}$ concentration. {*c*(curcumin) = 5 μM; pH = 6.8 (PBS' buffer); solvent: 95% water/5% ethanol; *T* = 25.0 °C; *I* = 0.2 M (KCl)}

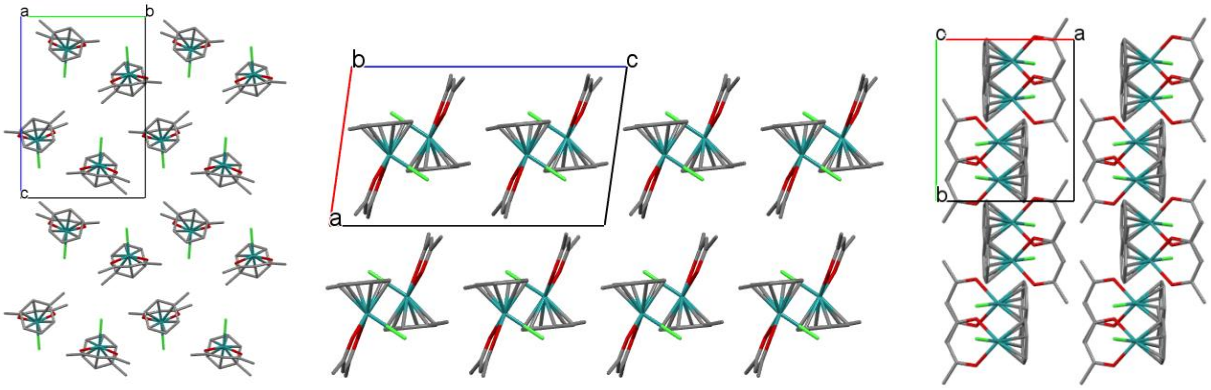
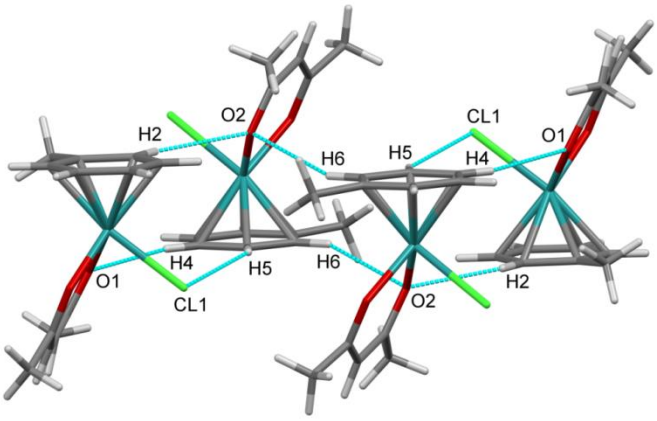


Figure S5. Packing arrangement in crystal $[Ru(\eta^6\text{-tol})(acac)Cl]$ (**1**) viewed from the *a*, *b* and *c* crystallographic directions. Hydrogen atoms are omitted for clarity.

a)



b)

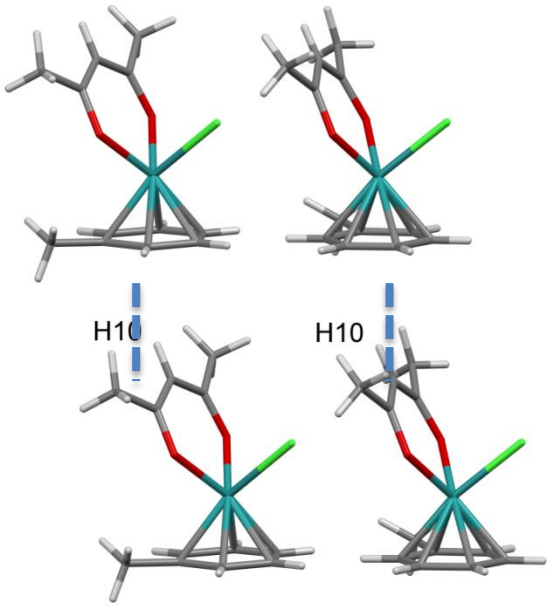


Figure S6. a) Packing arrangements and C-H…X and b) C10-H10…Cg interactions (with H...Cg distance 2.85 Å, C10-H10...Cg angle 156° and C10...Cg distance 3.734(8) Å) in crystal [Ru(η^6-tol)(acac)Cl] (**1**). Details of hydrogen bond parameters are collected in Table S2.

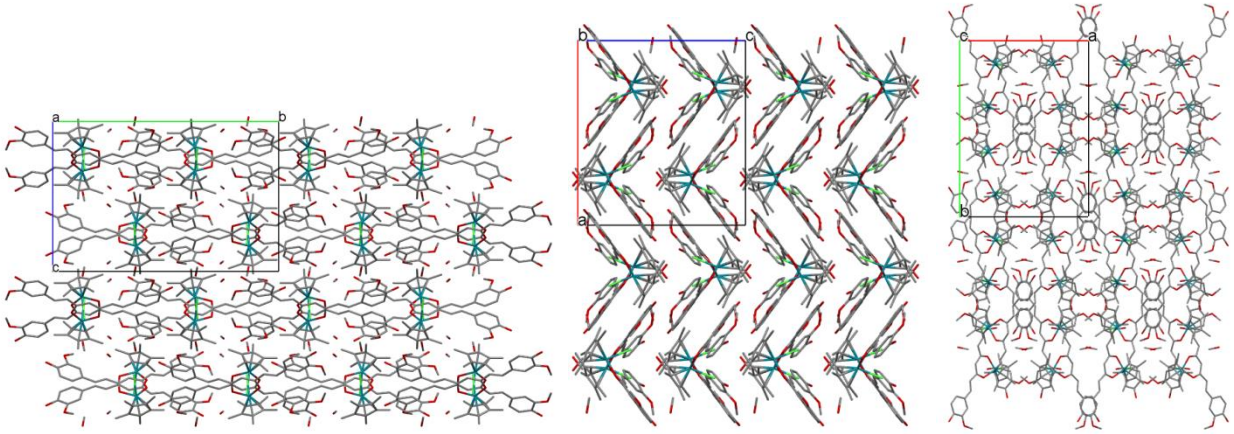


Figure S7. The crystal packing of crystal [Rh(η^5-C_5Me_5)(H_2curc)Cl] × 2MeOH (**2**) viewed from the *a*, *b* and *c* crystallographic axis, respectively. Hydrogen atoms are omitted for clarity.

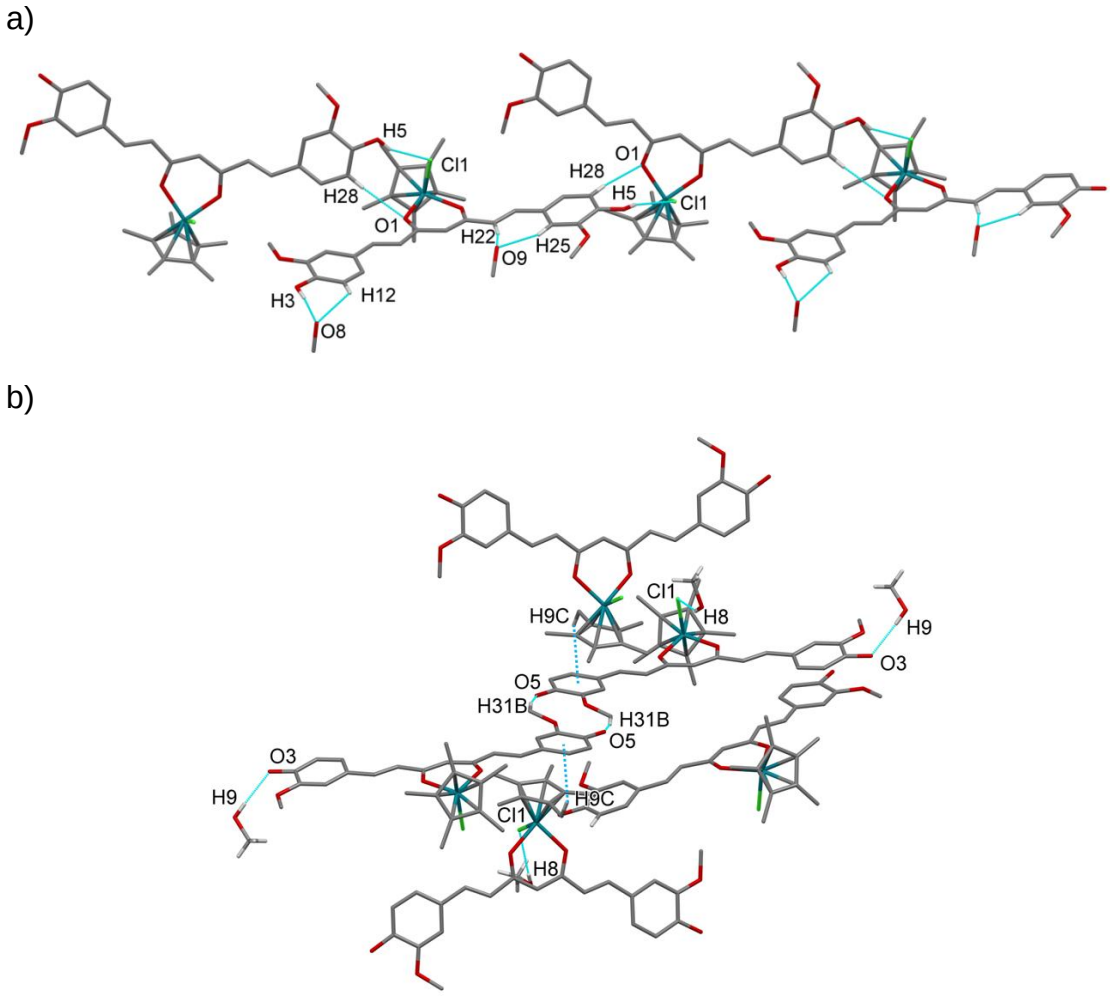


Figure S8. a) Packing arrangement showing the system of the hydrogen bonds in crystal [Rh(η^5-C_5Me_5)(H_2curc)Cl] × 2MeOH (**2**) viewed at the crystallographic direction *b* and b) direction *c*. Details of hydrogen bond parameters are collected in Table S3.

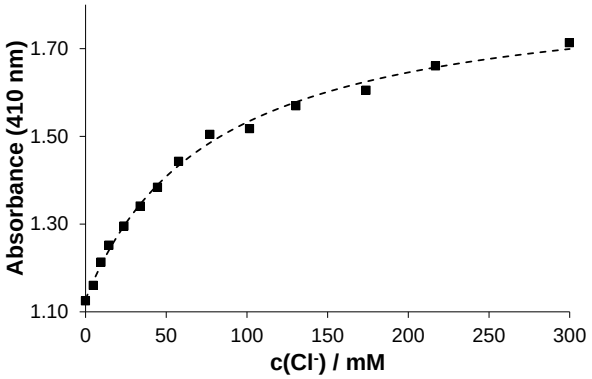


Figure S9. Measured (■) and fitted (- - -) absorbance values at 410 nm obtained from the absorption spectra of $[Rh(\eta^5\text{-}C_5Me_5)(acac)(H_2O)]^+$ in the presence of chloride ions at different concentrations. {$c([Rh(\eta^5\text{-}C_5Me_5)(H_2O)_3]^{2+})$ = c(acac) = 1 mM; $c(Cl^-)$ = 0 - 300 mM; pH = 7.30 (phosphate buffer); T = 25.0 °C}

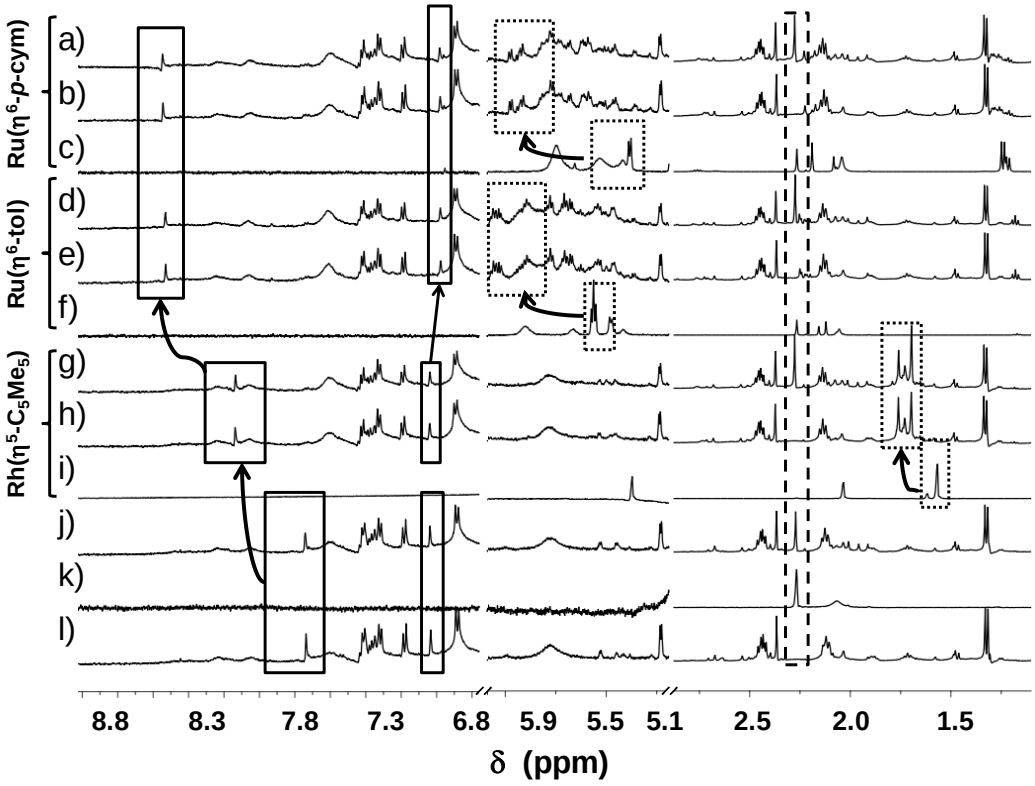


Figure S10. Monitoring of $[Rh(\eta^5\text{-}C_5Me_5)(acac)(H_2O)]^+$, $[Ru(\eta^6\text{-tol})(acac)(H_2O)]^+$ and $[Ru(\eta^6\text{-}p\text{-cym})(acac)(H_2O)]^+$ interaction with RPMI 1640 components, in 10% FBS medium by ^{1}H NMR spectroscopy. a) $[Ru(\eta^6\text{-}p\text{-cym})(acac)(H_2O)]^+$ in RPMI 1640 with 10% FBS medium; b) $[Ru(\eta^6\text{-}p\text{-cym})(H_2O)_3]^{2+}$ in RPMI 1640 with 10% FBS medium; c) $[Ru(\eta^6\text{-}p\text{-cym})(acac)(H_2O)]^+$ in buffered solution at pH = 7.40 (PBS'); d) $[Ru(\eta^6\text{-tol})(acac)(H_2O)]^+$ in RPMI 1640 with 10% FBS medium; e) $[Ru(\eta^6\text{-tol})(H_2O)_3]^{2+}$ in RPMI 1640 with 10% FBS medium; f) $[Ru(\eta^6\text{-tol})(acac)(H_2O)]^+$ in buffered solution at pH = 7.40 (PBS'); g) $[Rh(\eta^5\text{-}C_5Me_5)(acac)(H_2O)]^+$ in RPMI 1640 with 10% FBS medium; h) $[Rh(\eta^5\text{-}C_5Me_5)(H_2O)_3]^{2+}$ in RPMI 1640 with 10% FBS medium; i) $[Rh(\eta^5\text{-}C_5Me_5)(acac)(H_2O)]^+$ in buffered solution at pH = 7.4 (PBS'); j) acac in RPMI 1640 with 10% FBS medium; k) acac buffered solution at pH = 7.40 (PBS'); l) RPMI 1640 with 10% FBS medium. Dotted rectangles: C_5Me_5, toluene and p-cymene protons at various binding environment; dashed rectangle: free acac methyl groups; solid rectangles: His protons. {c(M) = c(acac) = 1 mM; solvent: 90% H_2O / 10% D_2O; T = 25.0 °C; t = 24 h}

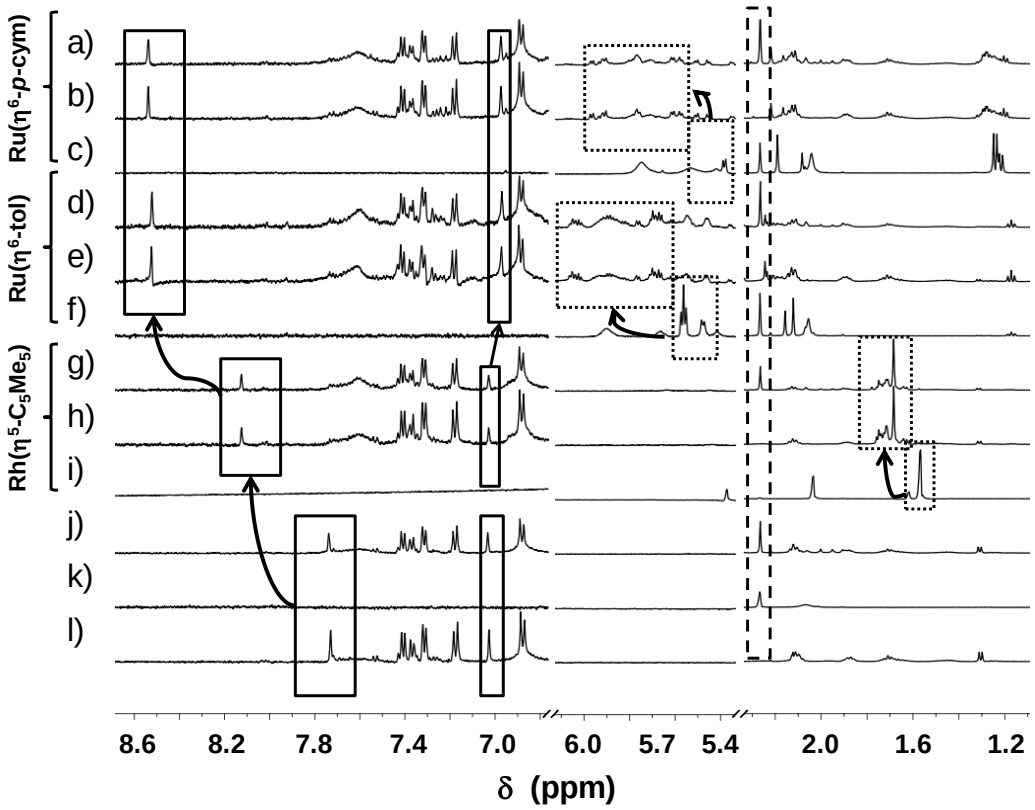


Figure S11. Monitoring of $[Rh(\eta^5\text{-}C_5Me_5)(acac)(H_2O)]^+$, $[Ru(\eta^6\text{-tol})(acac)(H_2O)]^+$ and $[Ru(\eta^6\text{-}p\text{-cym})(acac)(H_2O)]^+$ interaction with RPMI 1640 medium components by ^{1}H NMR spectroscopy. a) $[Ru(\eta^6\text{-}p\text{-cym})(acac)(H_2O)]^+$ in RPMI 1640 medium; b) $[Ru(\eta^6\text{-}p\text{-cym})(H_2O)_3]^{2+}$ in RPMI 1640 medium; c) $[Ru(\eta^6\text{-}p\text{-cym})(acac)(H_2O)]^+$ in buffered solution at pH = 7.40 (PBS'); d) $[Ru(\eta^6\text{-tol})(acac)(H_2O)]^+$ in RPMI 1640 medium; e) $[Ru(\eta^6\text{-tol})(H_2O)_3]^{2+}$ in RPMI 1640 medium; f) $[Ru(\eta^6\text{-tol})(acac)(H_2O)]^+$ in buffered solution at pH = 7.40 (PBS'); g) $[Rh(\eta^5\text{-}C_5Me_5)(acac)(H_2O)]^+$ in RPMI 1640 medium; h) $[Rh(\eta^5\text{-}C_5Me_5)(H_2O)_3]^{2+}$ in RPMI 1640 medium; i) $[Rh(\eta^5\text{-}C_5Me_5)(acac)(H_2O)]^+$ in buffered solution at pH = 7.40 (PBS'); j) acac in RPMI 1640 medium; k) acac buffered solution at pH = 7.40 (PBS'); l) RPMI 1640 medium. Dotted rectangles: C_5Me_5 and toluene and *p*-cymene protons at various binding environment; dashed rectangle: free acac methyl groups; solid rectangles: His protons. {*c*(M) = *c*(acac) = 1 mM; solvent: 90% H_2O / 10% D_2O; *T* = 25.0 °C; *t* = 24 h}

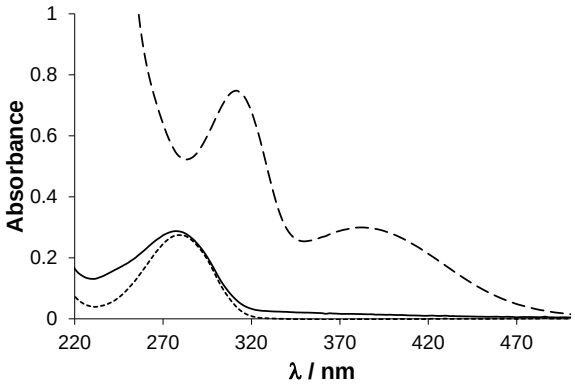


Figure S12. UV-Vis absorption spectra of samples after ultrafiltration: dashed line shows $[Rh(\eta^5\text{-}C_5Me_5)(acac)(H_2O)]^+$ sample (without the protein) before filtration, solid line shows filtrate of the HSA – $[Rh(\eta^5\text{-}C_5Me_5)(acac)(H_2O)]^+$ sample, dotted line shows filtrate of HSA – acac sample. {c(HSA) = 50 μM; c($[Rh(\eta^5\text{-}C_5Me_5)(acac)(H_2O)]^+$) = 150 μM; ℓ = 1 cm; T = 25.0 °C; I = 0.2 M (KCl)}