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The role of hydroxo-bridged dinuclear species and the influence of "innocent" buffers in the reactivity of *cis*-$[Co^{III}(cyclen)(H_2O)_2]^{3+}$ and $[Co^{III}(tren)(H_2O)_2]^{3+}$ complexes with biologically relevant ligands at physiological pH

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SUPPORTING INFORMATION

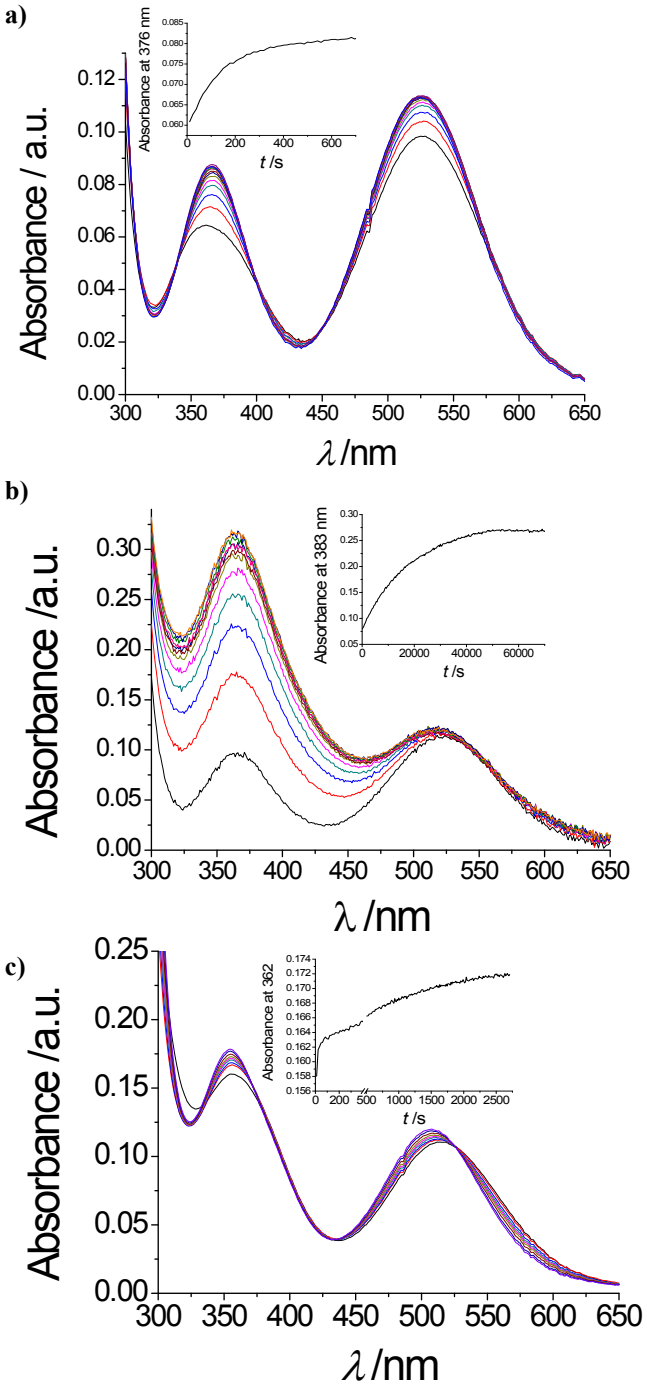


Figure S1.- a) Initial fast changes in the electronic spectrum at 25 ºC of a solution of *cis*-$[Co(cyclen)(H_2O)_2](CF_3SO_3)_3$ complex (1×10^{-3} M) in non-buffered aqueous solution at pH = 6.9 (I = 1.0 $NaClO_4$, 600 s); b) Consecutive slow changes for the same solution (50 ºC, 16 h); c) Changes in the

electronic spectrum at 25 ºC of a solution of $[Co(tren)(H_2O)_2](CF_3SO_3)_3$ complex (9×10^{-4} M) in non-buffered aqueous solution, pH = 7.2 (I = 1.0 $NaClO_4$, 40 minutes).

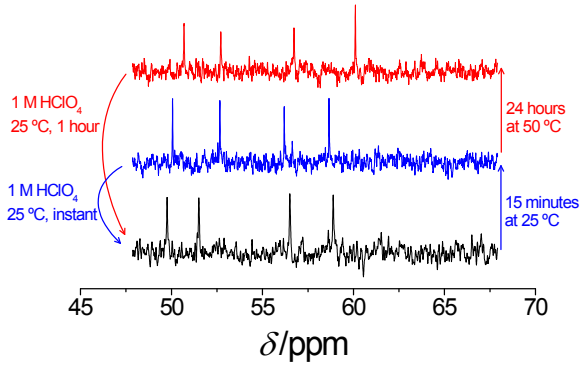
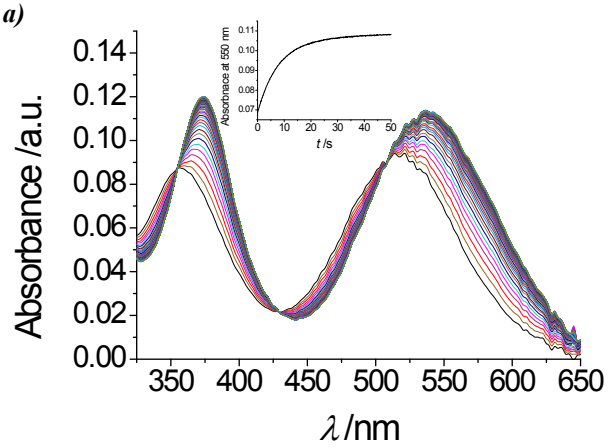


Figure S2.- ^{13}C NMR spectral changes observed during the reaction of *cis*-$[Co(cyclen)(H_2O)_2]^{3+}$ in alkaline solution in different conditions (pH =7.5).

a)



b)

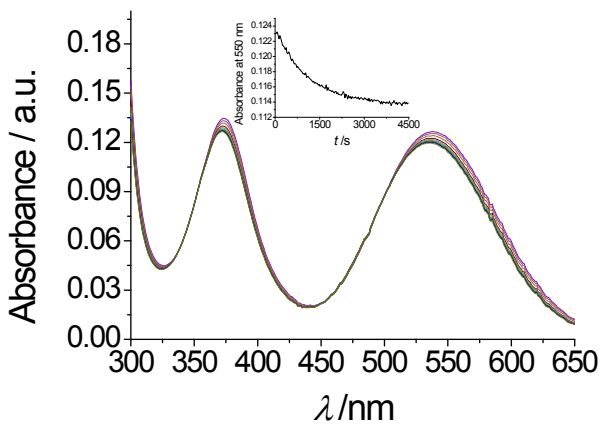


Figure S3.- Changes in the electronic spectrum at 25 ºC of a solution of *cis*-[Co(cyclen)$(H_2O)_2$]$(CF_3SO_3)_3$ complex (5×10^{-4} M) with 0.02 M NaH_2PO_4 in HEPES 0.4 M buffered aqueous pH = 7.0 (I = 1.0 $NaClO_4$). *a)* First step, 50 seconds; *b)* Second step, 4500 seconds.

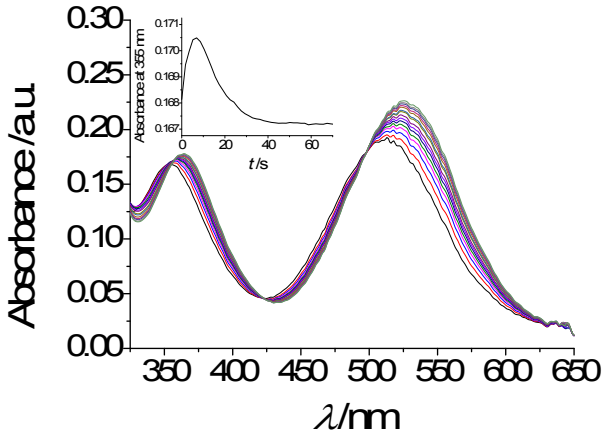


Figure S4.- Changes in the electronic spectrum at 25 ºC of a solution of *cis*-[Co(cyclen)$(H_2O)_2$]$(CF_3SO_3)_3$ complex (1×10^{-3} M) with 0.08 M 5'-CMP in 0.4 M HEPES buffered aqueous pH = 7.0 (I = 1.0 $NaClO_4$, 1 minute).

Table S1.- Values of the observed rate constants for the *cis*-$[Co(cyclen)(H_2O)_2]^{3+}$ + Ligand reactions studied as a function of the different variables used.

Ligand	Buffer	pH	*T* /°C	*P* /	10^3×[Co] /M	[Ligand] /M	k_{obs1} /	k_{obs2} /
OH^-	0.4 M HEPES	7.0	25	1	0.25	0.4	12[a]	[b]
					0.5	0.4	12 [a]	[b]
					1.0	0.4	13 [a]	[b]
5'-CMP	0.4 M HEPES	6.5	15	1	1.0	0.08	0.092	0.014
			20		1.0	0.08	0.14	0.021
			25		1.0	0.02	0.14	0.027
						0.03	0.19	0.028
						0.04	0.21	0.028
						0.06	0.23	0.029
						0.08	0.22	0.029
						0.1	0.24	0.029
			35		1.0	0.08	0.50	0.064
		7.0	15	1	1.0	0.08	0.11	0.020
			20		1.0	0.08	0.17	0.027
			25		1.0	0.02	0.15	0.035
						0.03	0.22	0.035
						0.04	0.25	0.036
						0.06	0.27	0.036
						0.08	0.29	0.037
				300		0.08	0.25	[b]
							0.22	[b]
				400			0.24	[b]
							0.23	[b]
				600			0.27	[b]
				750			0.27	[b]
							0.24	[b]
				900			0.26	[b]
				1200			0.24	[b]
						0.1	0.30	0.038
			35		1.0	0.08	0.56	0.095
		7.5	15	1	1.0	0.08	0.14	0.026
			20		1.0	0.08	0.22	0.041
			25		1.0	0.02	0.19	0.054
						0.03	0.26	0.056

						0.04	0.30	0.059
						0.06	0.33	0.059
						0.08	0.34	0.060
			35		1.0	0.08	0.82	0.20
$H_2PO_4^-/HPO_4^{2-}$	0.4 M HEPES	6.5	25	1	0.5	0.01	[b]	0.00093
		7.0	25	1	0.25	0.004	0.052	[b]
					0.25	0.006	0.070	[b]
					0.5	0.01	0.083	0.0010
					0.25	0.015	0.10	[b]
					0.5	0.015	0.099	[b]
					0.5	0.02	0.11	0.0010
					0.5	0.025	0.11	[b]
		7.5	25	1	0.5	0.01	[b]	0.0013

[a] Derived from a 2×A≮B fitting, in $M^{-1}s^{-1}$. [b] Not determined.