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Mechanistic Aspects of the Chemistry of Mononuclear Cr^{III} complexes with Pendant-arm Macrocyclic Ligands and Formation of Discrete Cr^{III}/Fe^{II} and $Cr^{III}/Fe^{II}/Co^{III}$ Cyano-Bridged Mixed Valence Compounds.

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Supplementary material:

Table S1.- Observed rate constants for the reactions studied as a function of reactants, concentrations, pH, temperature and pressure.

Figure S1.- Eyring plot for the slow process observed on solution of the $[CrL_{15}Cl]^{2+}$ complexes depending on the starting material.

Figure S2.- Uv-vis changes of the spectrum of a solution of the dinuclear complex $[\{(H\boldsymbol{L}_{15})(H_2O)Cr^{III}NC\}Fe^{II}(CN)_5]$, 4×10^{-4} M, with $S_2O_8^{2-}$, 45×10^{-3} M, at pH = 4 and 25 ºC.

Figure S3.- Electronic spectrum changes of a solution of complex *cis*-$[\{(\boldsymbol{L}_{15})(OH)Cr^{III}NC\}\{cis\text{-}V\text{-}L_{13}Co^{III}NC\}Fe^{II}(CN)_4]^+$ with pH.

Kinetics of the *trans-II* or *trans-III*-$[CrClL_{15}]^2$ reaction at pH 9.-

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Table S1.- Observed rate constants for the reactions studied as a function of reactants, concentrations, pH, temperature and pressure.

Reaction	*T* /K	P /atm	$[OH^-]$ /M	pH	$10^3\times[Cr^{III}]$ /M	$10^3\times[Fe^{II}]$ /M	$10^4\times k_{obs}$ /s^{-1}
trans-II-$[Cr^{III}(OH)L_{15}]^{2+}$	303	1	0.10		0.40		0.18
to *trans*-$[Cr^{III}(OH)_2(\boldsymbol{L}_{15})]^+$	313	1					0.90
	323	1					1.8
	327	300					3.2
		600					3.0
		900					2.8
		1200					2.6
	333	1					6.9
	333	1	0.05				7.1
	333	1	0.15				6.8
	338	1	0.10				8.4
trans-III-$[Cr^{III}(OH)L_{15}]^{2+}$	303	1	0.10		0.40		0.19
to *trans*-$[Cr^{III}(OH)_2(\boldsymbol{L}_{15})]^+$	313	1					6.3
	323	1					2.1
	333	1					7.3
	333	1	0.05				7.0
	333	1	0.15				7.4
transII/III-$[Cr^{III}ClL_{15}]^{2+}$	303	1		4.0	0.50	5.0	0.40
plus $[Fe(CN)_6]^{4-}$						10	0.80
						20	1.5
						40	2.6
						100	6.9
	308	300			0.25	8.0	0.62
						30	1.4
						80	2.5
						120	3.2
		600				8.0	0.30
						40	1.2
						80	2.0
						150	2.8
		900				8.0	0.25

						40	1.0
						80	1.6
						150	2.2
		1200				8.0	0.17
						40	0.9
						80	1.4
						150	1.8
	313	1			0.50	5.0	1.0
						10	2.3
						20	4.6
						40	9.5
						100	23
	323	1				5.0	6.5
						10	14
						20	26
						40	44
						100	100
	333	1				5.0	11
						10	25
						20	53
						40	95
						100	230
					0.5	20	49
						40	120
trans-$[Cr^{III}(OH)_2(\boldsymbol{L}_{15})]^+$	323	1		9.0	0.5	2.5	0.096
plus $[Fe(CN)_6]^{4-}$						5.0	0.12
						7.0	0.14
						10	0.16
						15	0.19
						20	0.20
						30	0.21
						40	0.25
	333	1				5.0	0.42
						7.0	0.48
						10	0.59
						15	0.67

						20	0.71
		1			5.0	0.5	0.38
					7.0		0.41
					10		0.53
					15		0.61
					20		0.68
	343	1				5.0	1.0
						7.0	1.2
						10	1.4
						15	1.5
						20	1.7
	353	1				5.0	2.6
						7.0	3.1
						10	3.4
						15	3.7
						20	3.9
						40	4.3
	346	300			0.50	58	3.2
						80	3.3
		600				29	3.5
						60	3.6
		900				3.0	1.2
						29	2.8
						58	3.7
						80	3.8
		1200				58	4.2
						80	4.0
		1500				58	4.7
						80	4.6
trans-$[Cr^{III}(OH)_2(\boldsymbol{L}_{15})]^+$ plus	323	1		9.0	0.10	0.50	2.3
$[\{cis\text{-}V\text{-}L_{13}Co^{III}NC\}Fe^{II}(CN)_5]^-$						1.0	2.7
						2.5	3.0
						5.0	3.4
						10	3.7
						20	3.9
	333					0.50	4.9

						1.0	5.2
						2.5	6.2
						5.0	6.9
						10	8.1
						20	9.0
	343					0.50	5.6
						1.0	7.3
						2.5	10
						5.0	12
						10	15
						20	18
	353					0.50	8.7
						1.0	11
						2.5	14
						5.0	23
						10	28
						20	31

s.p.6

Figure S1.- Eyring plot for the slow process observed on solution of the $[CrL_{15}Cl]^{2+}$ complexes depending on the starting material.

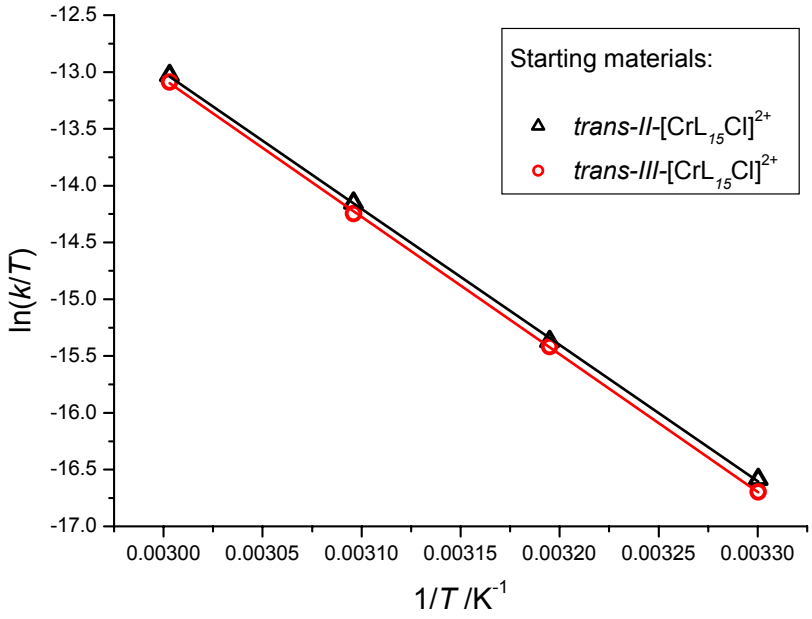


Figure S2.- Uv-vis changes of the spectrum of a solution of the dinuclear complex $[\{(H\boldsymbol{L}_{15})(H_2O)Cr^{III}NC\}Fe^{II}(CN)_5]$, 4×10^{-4} M, with $S_2O_8^{2-}$, 45×10^{-3} M, at pH = 4 and 25 ºC.

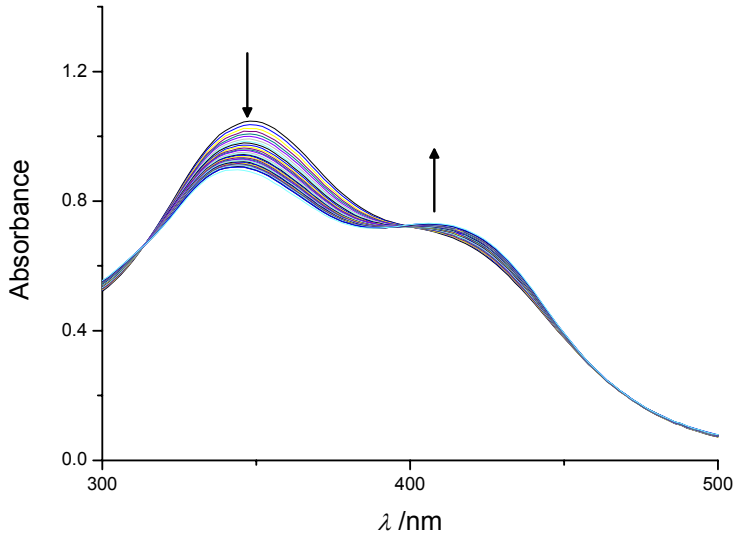
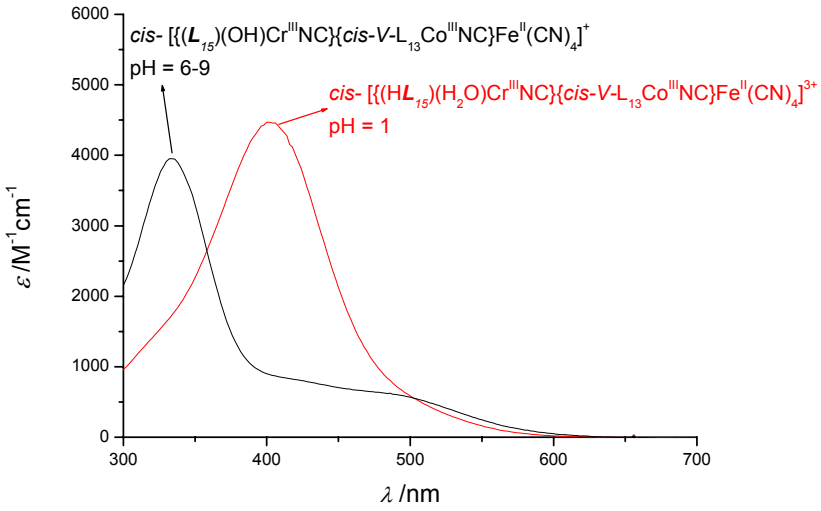


Figure S3.- Electronic spectrum changes of a solution of complex *cis*-[{(***L***$_{15}$)(OH)Cr^{III}NC}{*cis*-*V*-L$_{13}$Co^{III}NC}Fe^{II}(CN)$_4$]$^+$ with pH.



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Kinetics of the *trans-II* or *trans-III*-[CrClL$_{15}$]^{2} reaction at pH 9.-

The values of the kinetic and activation parameters obtained for the process carried out with any of the two starting materials (*trans-II* or *trans-III*, Figure S1) at [OH^-] = 0.1 M are $^{323}k = 2.2\times10^{-4}$ s^{-1}, $\Delta H^{\ddagger} = 106\pm1$ kJ/mol, $\Delta S^{\ddagger} = -6\pm3$ J K/mol , $\Delta V^{\ddagger} = 6.3\pm0.5$ cm^3mol^{-1} (327 K) and independent of the value of [OH^-] in the 0.05-0.15 M range, as expected from the trends observed in previous literature. The large enthalpy value is the expected for a dissociatively activated conjugate base mechanism. As for $\Delta S^{\ddagger}$, the zero value obtained does not agree with a simple dissociation of the ligand, nevertheless organization of the solvent in these systems, including hydrogen bonding between the dangling amine and the entering water ligand, can be held responsible for the shift to more negative values, as well as for the increased discrimination (RNH_2/OH^-) observed with respect to the Co^{III} analogues. Finally, the values determined for $\Delta V^{\ddagger}$ are also definitively less positive than expected for similar processes which possibly indicates a certain compression of the entering aqua ligand *via* hydrogen bonding to the generated dangling amine group.