

Supporting Information

Ligand Sequential Replacement on Chromium(III)-Aqua Complexes by L-Alanine and Other Biological Amino Acids: A Kinetic Perspective

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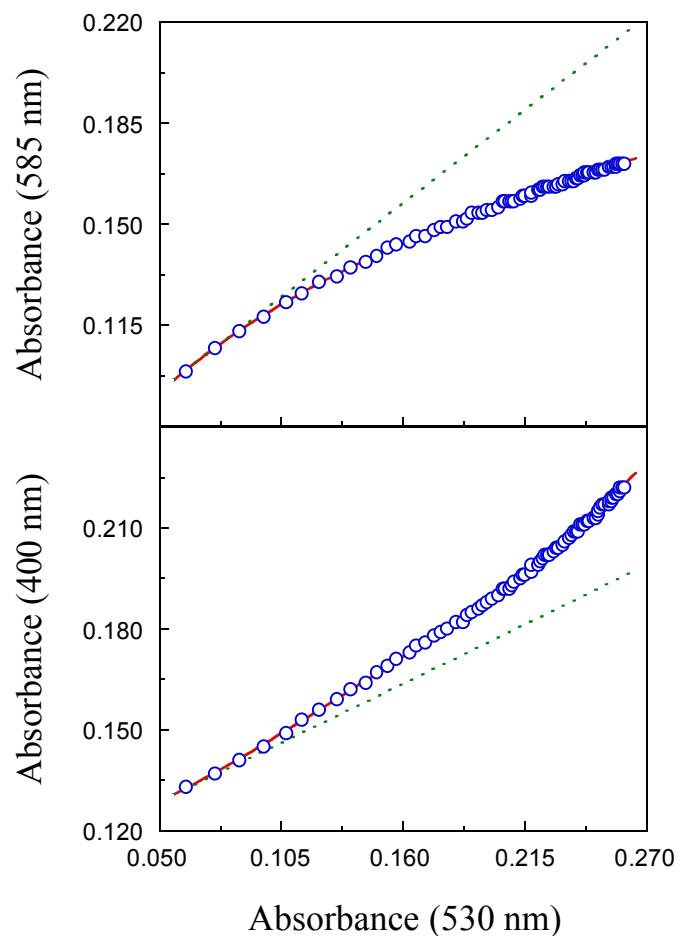


Figure S1. Absorbances at 585 (top) and 400 (bottom) nm as a function of the absorbance at 530 nm during the course of the reaction. $[\text{Cr}(\text{NO}_3)_3]_0 = 5.88 \times 10^{-3}$ M, $[\text{L-alanine}]_0 = 0.133$ M, $[\text{KOH}]_0 = 8.28 \times 10^{-3}$ M, $\text{pH}_\infty 3.97$, 25.0°C .

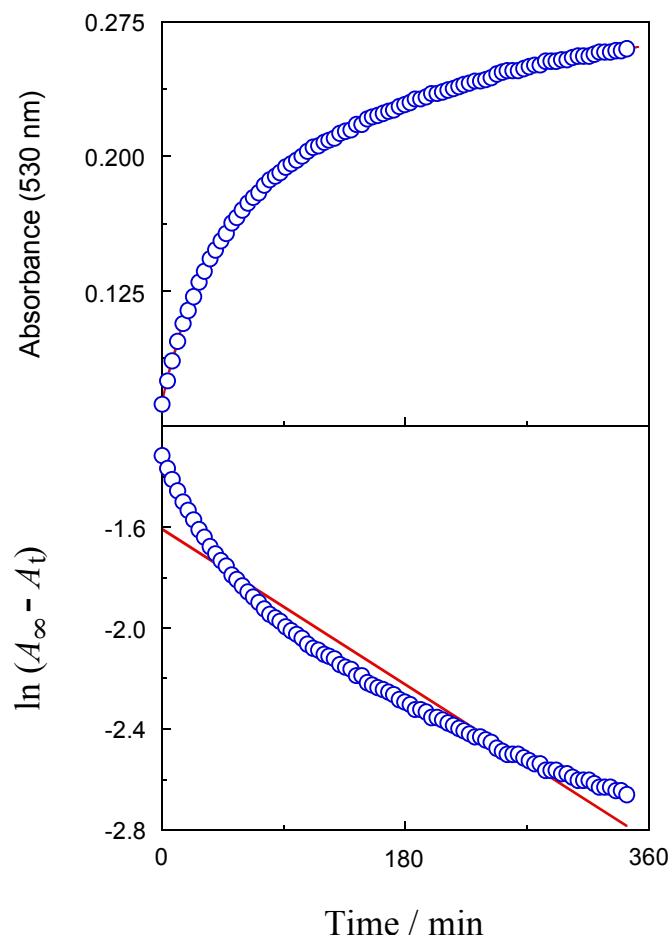


Figure S2. Absorbance at 530 nm as a function of time (top) and attempted pseudo-first order plot (bottom). $[\text{Cr}(\text{NO}_3)_3]_0 = 5.88 \times 10^{-3}$ M, $[\text{L-alanine}]_0 = 0.133$ M, $[\text{KOH}]_0 = 8.28 \times 10^{-3}$ M, $\text{pH}_\infty = 3.97$, 25.0°C .

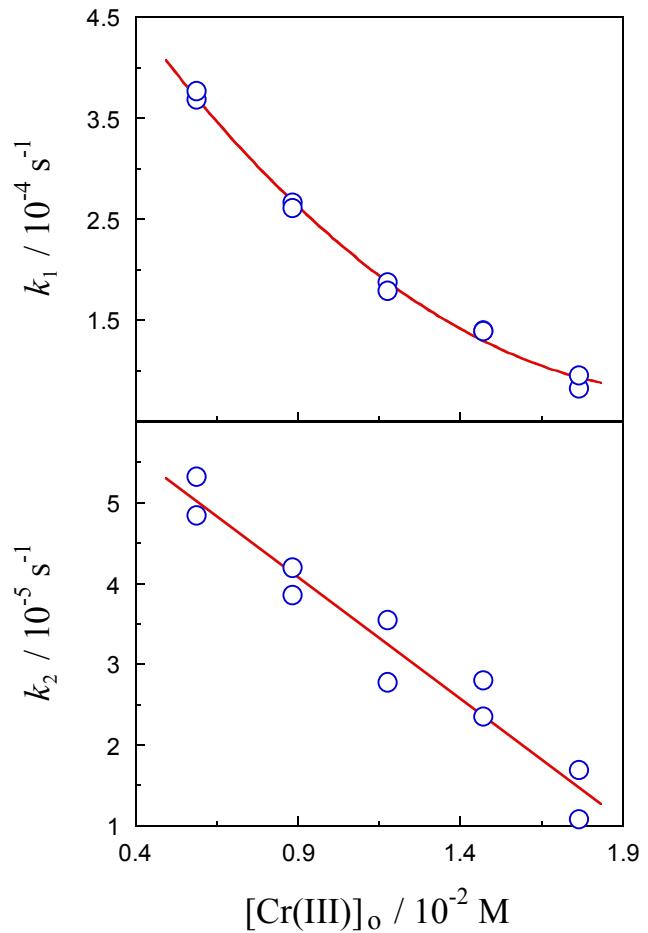


Figure S3. Dependence of the experimental rate constants k_1 (top, $r = 0.998$) and k_2 (bottom, $r = 0.972$) on the initial concentration of metal ion. $[Cr(NO_3)_3]_o = (0.59 - 1.76) \times 10^{-2} M$, $[L\text{-alanine}]_o = 0.354 M$, $[KOH]_o = 5.03 \times 10^{-3} M$, $pH_\infty = 3.72 - 4.12$, $25.0^\circ C$.

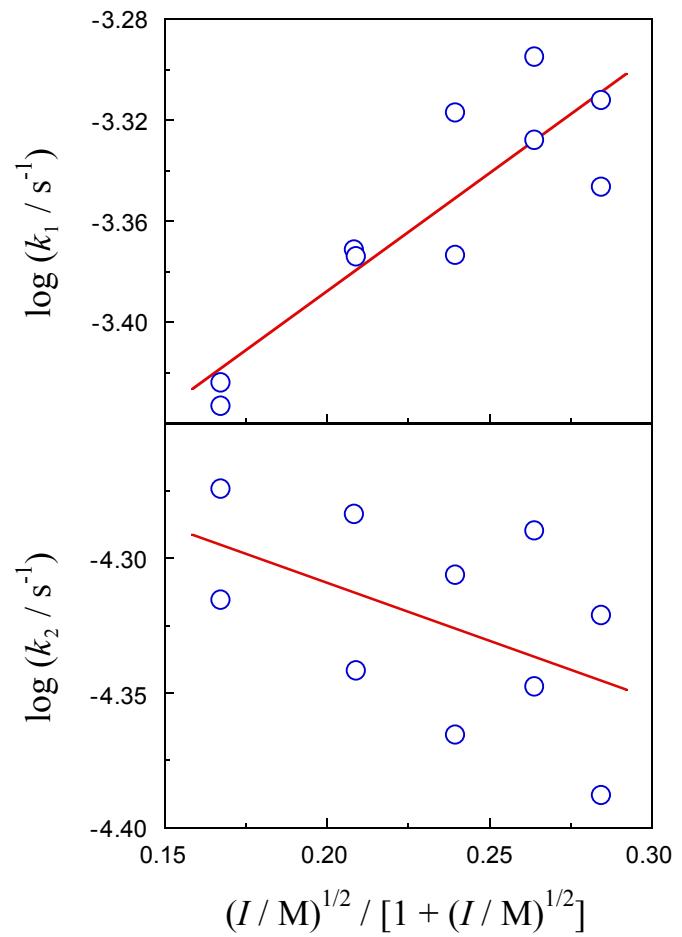


Figure S4. Dependence of experimental rate constants k_1 (top, $r = 0.876$) and k_2 (bottom, $r = 0.507$) on the medium ionic strength. $[\text{Cr}(\text{NO}_3)_3]_0 = 5.88 \times 10^{-3}$ M, $[\text{L-alanine}]_0 = 0.354$ M, $[\text{KOH}]_0 = 5.03 \times 10^{-3}$ M, $[\text{KNO}_3] = 0.000\text{--}0.118$ M, $\text{pH}_\infty = 4.12\text{--}4.20$, 25.0°C .

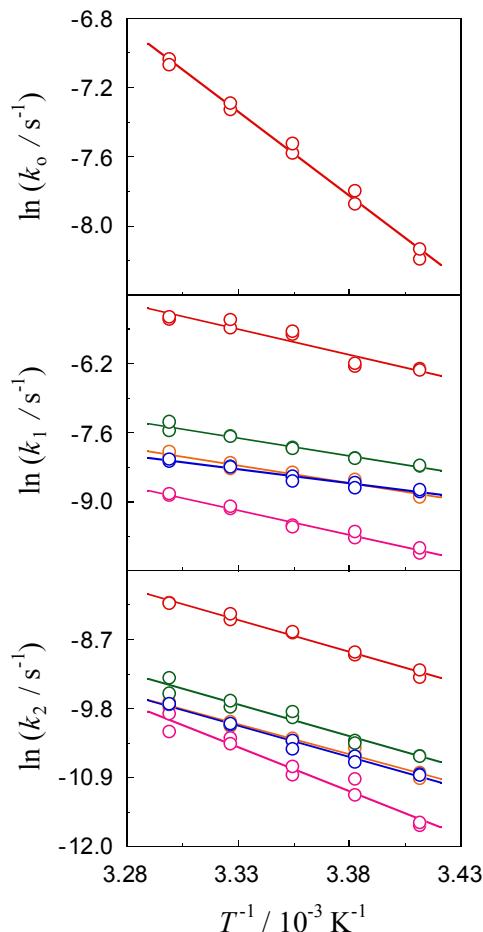


Figure S5. Dependence of the experimental rate constants on temperature for the reactions of $\text{Cr}(\text{NO}_3)_3$ (5.88×10^{-3} M) with five biological amino acids at $20.0\text{--}30.0$ °C.

Orange: $[\text{glycine}]_o = 0.194$ M, $[\text{KOH}]_o = 4.99 \times 10^{-3}$ M, $\text{pH}_\infty 3.86 \pm 0.07$, $r = 0.981$ (k_1) and 0.989 (k_2). Green: $[\text{L-alanine}]_o = 0.354$ M, $[\text{KOH}]_o = 5.03 \times 10^{-3}$ M, $\text{pH}_\infty 4.06 \pm 0.03$, $r = 0.988$ (k_1) and 0.981 (k_2). Violet: $[\text{L-phenylalanine}]_o = 8.82 \times 10^{-2}$ M, $[\text{KOH}]_o = 4.97 \times 10^{-3}$ M, $\text{pH}_\infty 3.58 \pm 0.02$, $r = 0.990$ (k_1) and 0.979 (k_2). Blue: $[\text{L-threonine}]_o = 0.194$ M, $[\text{KOH}]_o = 5.01 \times 10^{-3}$ M, $\text{pH}_\infty 3.60 \pm 0.05$, $r = 0.979$ (k_1) and 0.992 (k_2). Red: $[\text{L-histidine}]_o = 0.119$ M, $[\text{HCl}]_o = 9.55 \times 10^{-2}$ M, $\text{pH}_\infty 4.45 \pm 0.06$, $r = 0.996$ (k_o), 0.952 (k_1), and 0.993 (k_2).

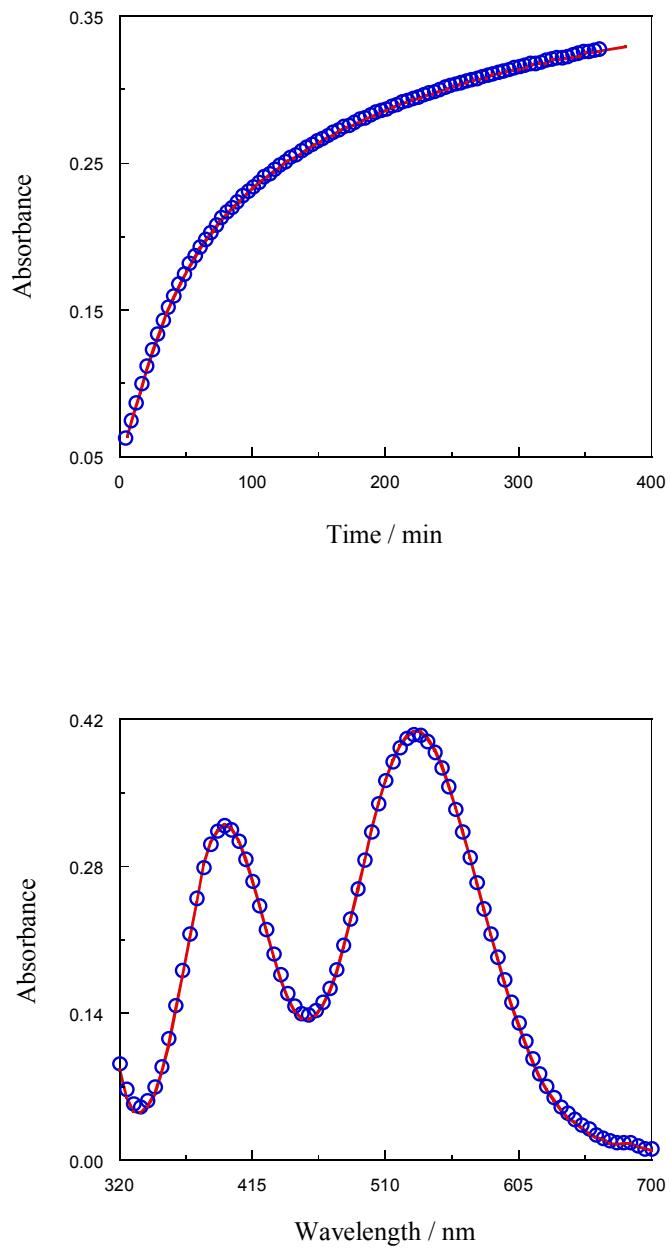


Figure S6. Absorbance at 530 nm as a function of time (top) and final UV-Vis spectrum (bottom) with either L-alanine (blue points) or DL-alanine racemic mixture (red line) as source of organic ligands. $[Cr(NO_3)_3]_o = 5.88 \times 10^{-3}$ M, $[ligand]_o = 0.354$ M, $[KOH]_o = 5.00 \times 10^{-3}$ M, $pH_\infty 4.10 \pm 0.02$, $25.0^\circ C$.

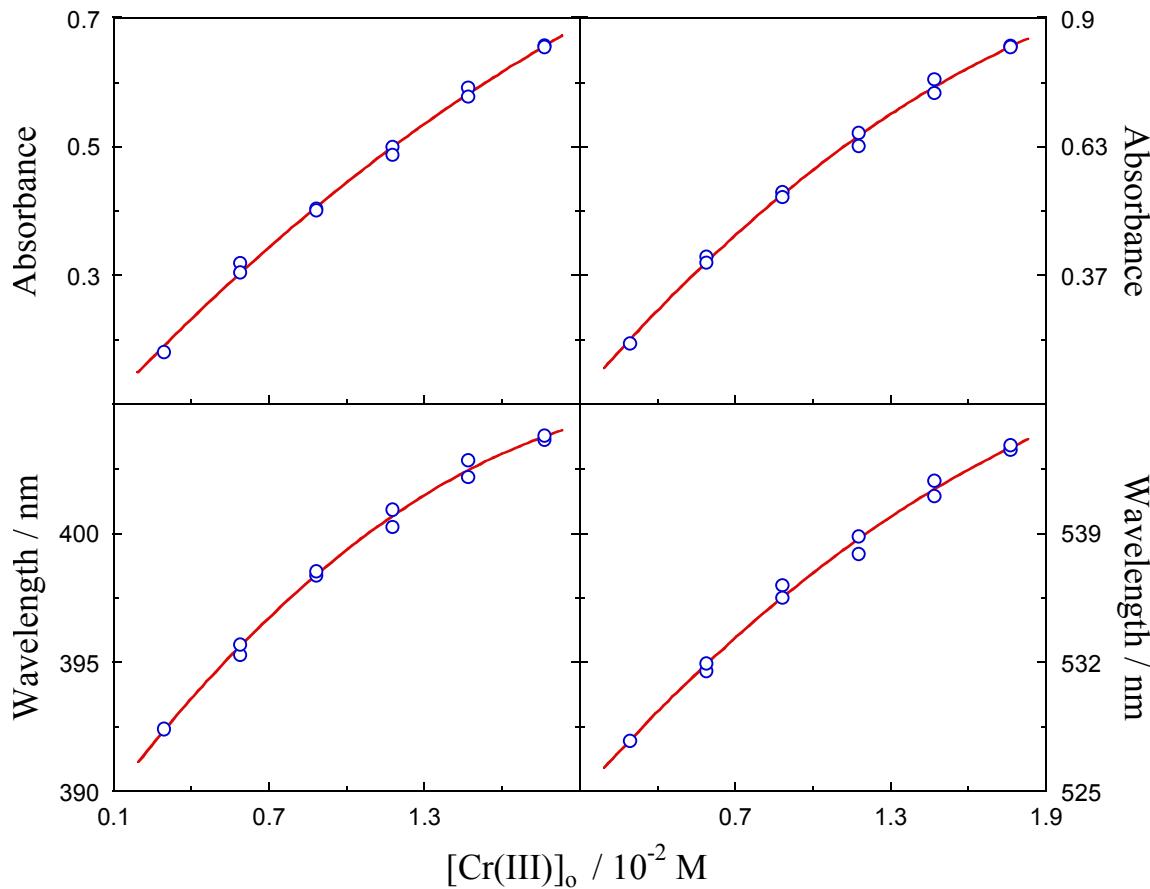


Figure S7. Wavelengths (bottom) and absorbances (top) corresponding to the first (left) and second (right) peaks of the electronic spectrum recorded for the final violet complex as a function of the metal ion initial concentration. $[\text{Cr}(\text{NO}_3)_3]_o = (0.29 - 1.76) \times 10^{-2}$ M, $[\text{L-alanine}]_o = 0.354$ M, $[\text{KOH}]_o = 5.03 \times 10^{-3}$ M, $\text{pH}_\infty 3.72 - 4.12$, 25.0°C .

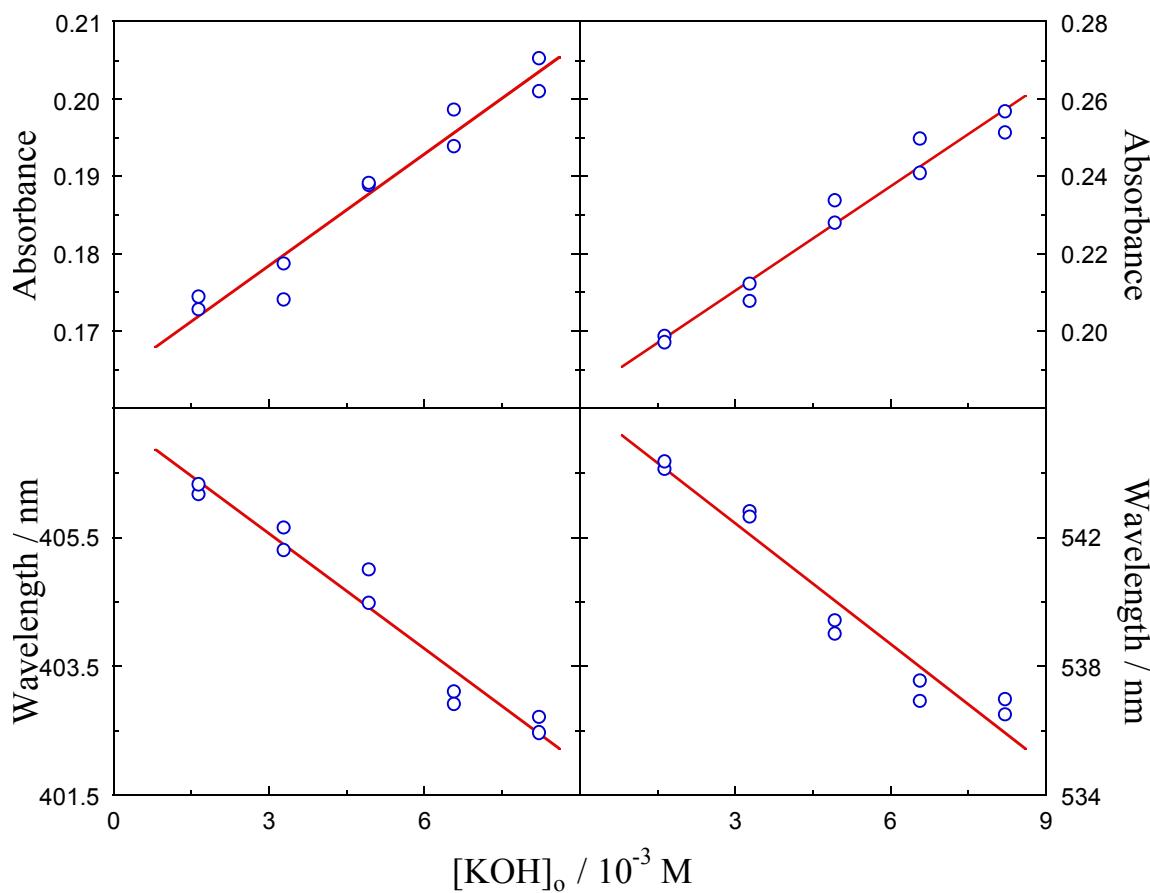


Figure S8. Wavelengths (bottom) and absorbances (top) corresponding to the first (left) and second (right) peaks of the electronic spectrum recorded for the final violet complex as a function of the potassium hydroxide initial concentration. $[\text{Cr}(\text{NO}_3)_3]_0 = 5.88 \times 10^{-3}$ M, $[\text{L-alanine}]_0 = 5.89 \times 10^{-2}$ M, $[\text{KOH}]_0 = (1.64 - 8.21) \times 10^{-3}$ M, pH_∞ 3.55 – 3.84, 25.0 °C.

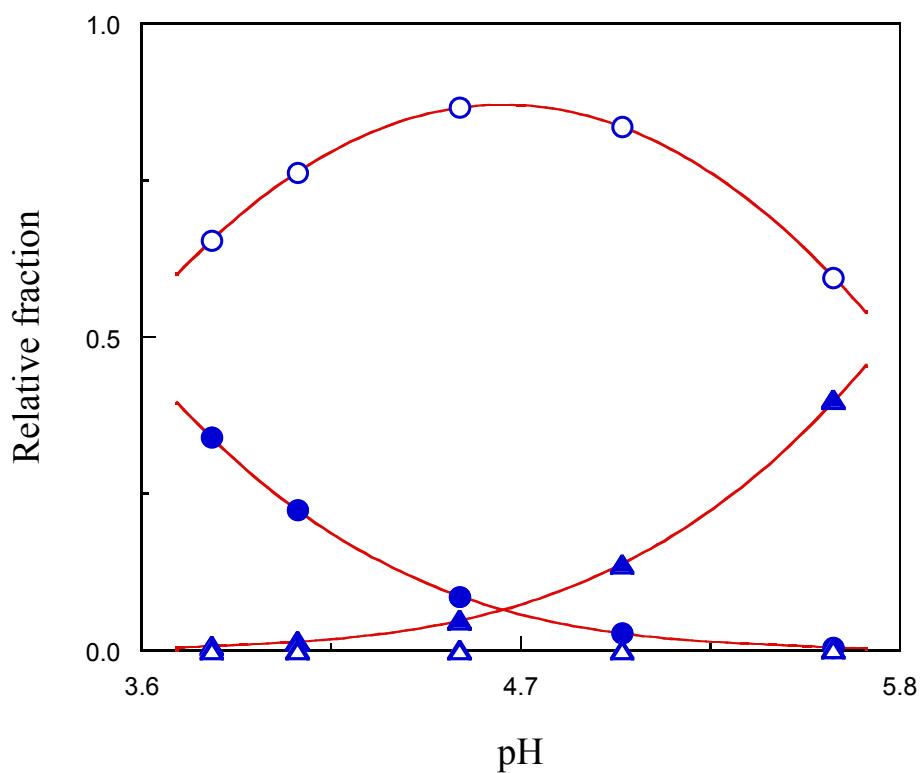


Figure S9. Relative fractions of $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ (filled circles), $[\text{Cr}(\text{OH})(\text{H}_2\text{O})_5]^{2+}$ (empty circles), $[\text{Cr}(\text{OH})_2(\text{H}_2\text{O})_4]^+$ (filled triangles), and $\text{Cr}(\text{OH})_3$ (empty triangles) at 25.0 °C as a function of the pH.