

## Versatility and trends in the interaction between Pd(II) and peptidehydroxamic acids

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### Supporting Information

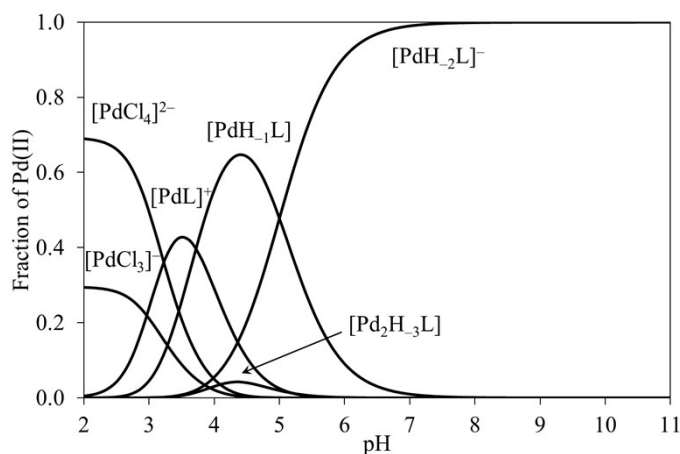


Fig. S1 Concentration distribution curves for Pd(II)-Ala-Gly-Gly-NHOH = 1:1 system at  $c_{\text{Pd(II)}} = 20 \mu\text{M}$  and  $c_{\text{Cl}^-} = 100 \text{mM}$

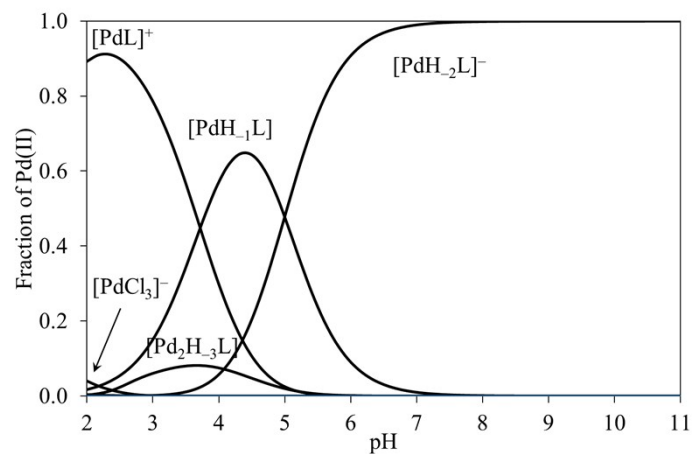


Fig. S2 Concentration distribution curves for Pd(II)-Ala-Gly-Gly-NHOH = 1:1 system at  $c_{\text{Pd(II)}} = 20 \mu\text{M}$  and  $c_{\text{Cl}^-} = 4 \text{ mM}$

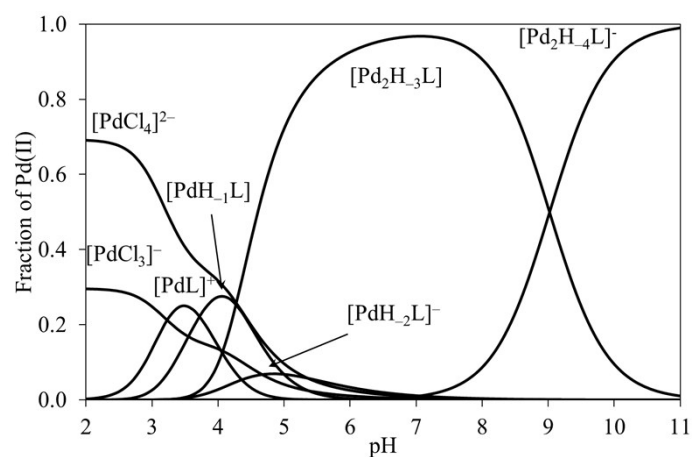


Fig. S3 Concentration distribution curves for Pd(II)-Ala-Gly-Gly-NHOH = 2:1 system at  $c_{\text{Pd(II)}} = 20 \mu\text{M}$  and  $c_{\text{Cl}^-} = 100 \text{ mM}$

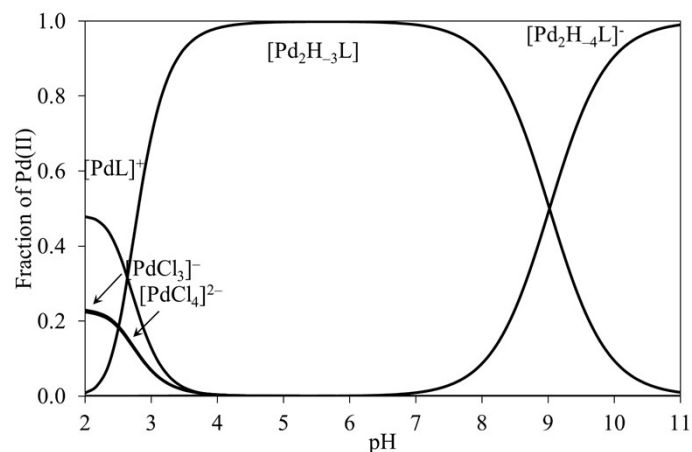


Fig. S4 Concentration distribution curves for Pd(II)-Ala-Gly-Gly-NHOH = 2:1 system at  $c_{\text{Pd(II)}} = 20 \mu\text{M}$  and  $c_{\text{Cl}^-} = 4 \text{ mM}$

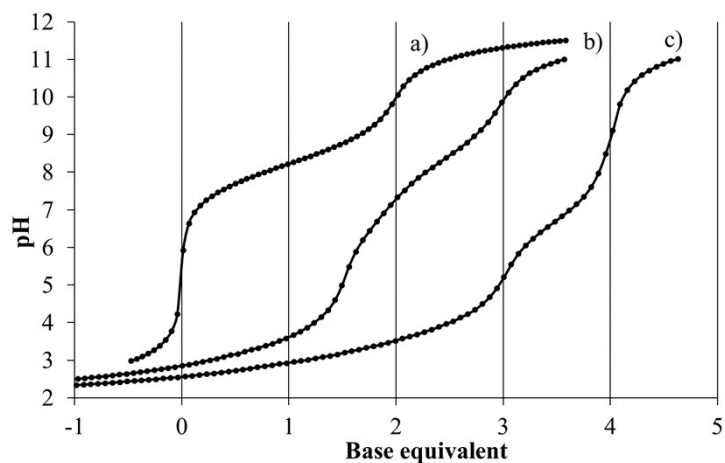


Fig. S5 Representative titration curves of  $\text{H}^+$ -Ala-Gly-Gly-N(Me)OH (a) and Pd(II)-Ala-Gly-Gly-N(Me)OH systems at 1:2 ratio (b), 1:1 ratio (c)

Table S6 NMR samples prepared for Pd(II)-Ala-Gly-Gly-N(Me)OH system at different metal ion to ligand ratios and pH values

Duration	pH	
	$c_M:c_L = 1:1$	$c_M:c_L = 1:2$
1 hour	1.93	2.19
	2.25	2.49
	2.53	2.98
	4.05	3.69
	6.46	6.03
	7.20	7.00
	8.10	7.82
	9.60	9.25
	12.0	10.8
24 hours	1.93	2.19
	2.25	2.49
	2.53	2.98
	4.05	3.69
	6.46	6.03
	7.20	7.00
	8.10	7.82
	9.60	9.25
	12.0	10.8
5 days		2.19
		2.49
		2.98
	2.53	3.69
	4.05	6.03
	8.10	7.00
		7.82
		9.25
		10.8
7 days		2.19
		2.49
		2.98
		3.69
		6.03
		7.00
		7.82
		9.25
		10.8
9 days	2.53	
	4.05	
	8.10	

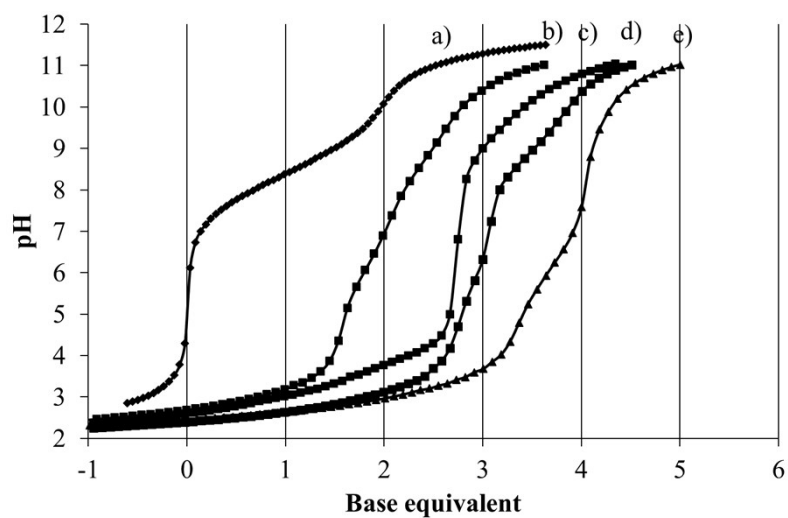


Fig. S7 Representative titration curves of  $\text{H}^+$ –Ala-Ala-NHOH (a) and Pd(II)–Ala-Ala-NHOH systems at 1:2 ratio (b), 1:1 ratio (d), 1.5:1 ratio (e) and the back-titrated sample at 1:1 metal ion to ligand ratio after 4 days (c)

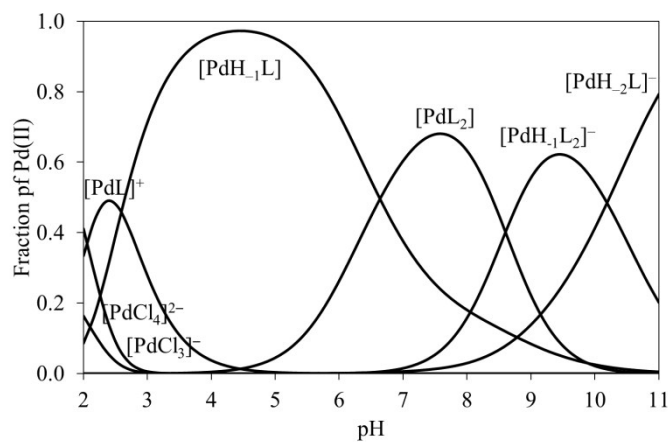
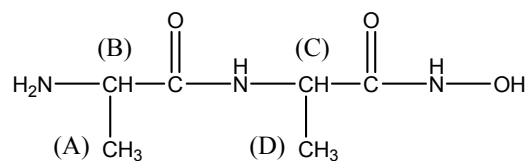


Fig. S8 Concentration distribution curve for Pd(II) – Ala-Ala-NHOH system at  $c_{\text{lig}} = 3 \text{ mM}$  and  $c_{\text{Pd(II)}} = 1.5 \text{ mM}$

Table S9 Chemical shifts ( $\delta$ ) in ppm determined in the Pd(II)-Ala-Ala-NHOH system at different metal ion to ligand ratios and pH values



Ratio ( $c_{\text{Pd(II)}}:c_{\text{L}}$ )	pH	(A)	(D)	(C)	(B)	Main species
"free" ligand	2.00	1.533	1.392	4.263	4.084	$\text{H}_2\text{L}^+$
	7.39	1.431	1.384	4.253	3.875	$\text{H}_2\text{L}^+/\text{HL}$
	8.44	1.284	1.356	4.238	3.573	HL
	9.67	1.241	1.323	4.231	3.476	$\text{HL}/\text{L}^-$
	10.90	1.236	1.319	4.230	3.469	$\text{L}^-$
1:1	2.04	1.533	1.392	4.263	4.084	$\text{H}_2\text{L}^+$
		1.381	1.300	4.141	3.631	$[\text{PdL}]^{2-} / [\text{PdH}_1\text{L}]^{2-}$
	7.35	1.329	1.295	3.881	3.587	$[\text{PdH}_1\text{L}]^{2-}$
	9.51	1.329	1.295	3.881	3.587	$[\text{PdH}_1\text{L}]^{2-}$
1.5:1		1.286	1.264	3.749	3.526	$[\text{PdH}_2\text{L}]^{2-}$
	2.40	1.533	1.392	4.263	4.084	$\text{H}_2\text{L}^+$
		1.362	1.299	4.041	3.614	$[\text{PdL}]^{2-} / [\text{PdH}_1\text{L}]^{2-}$
	4.90	1.329	1.302	3.881	3.588	$[\text{PdH}_1\text{L}]^{2-}$
		1.286	1.280	4.015	3.556	$[\text{Pd}_3\text{H}_4\text{L}_2]^{2-}$
	7.06	1.286	1.280	4.015	3.556	$[\text{Pd}_3\text{H}_4\text{L}_2]^{2-}$

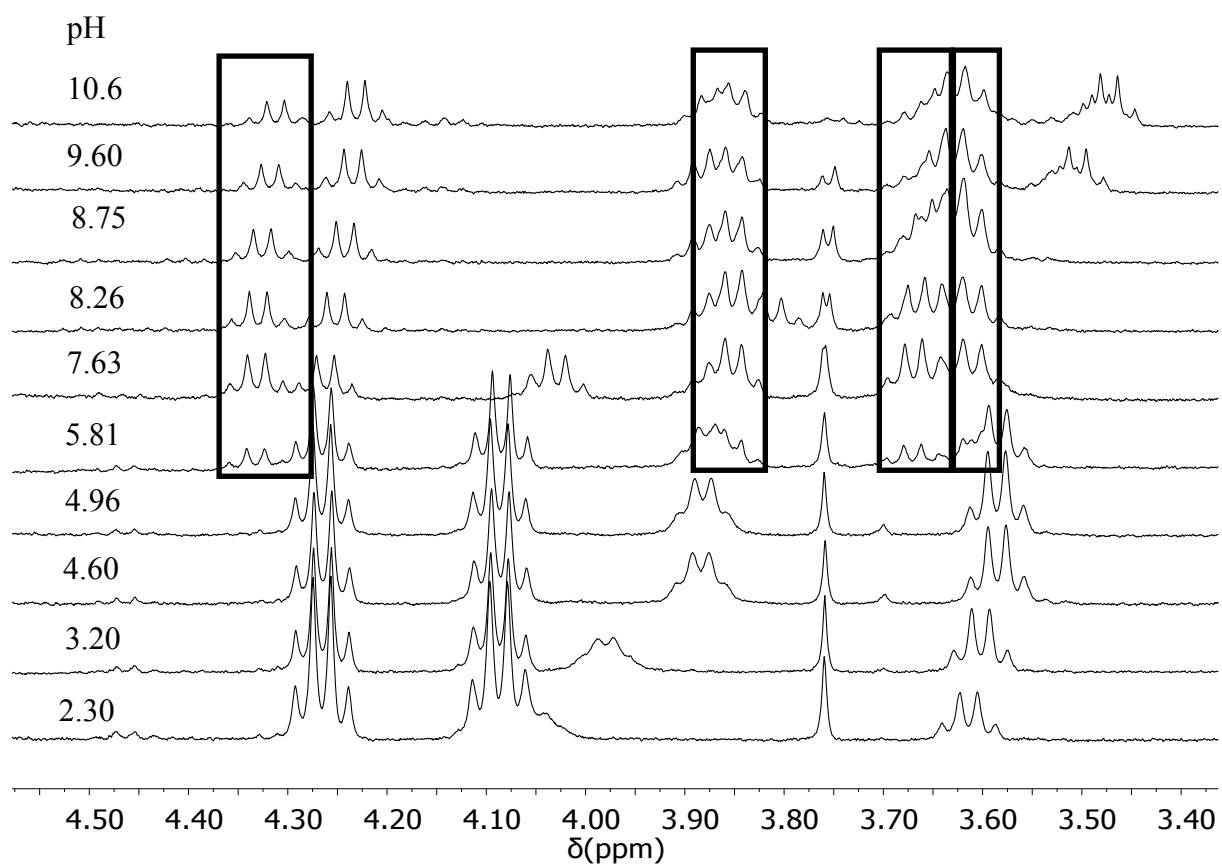


Fig. S10  $^1\text{H}$  NMR spectra of Pd(II)-Ala-Ala-NHOH system at 1:2 metal ion to ligand ratio at different pH values (signals of the bis-complexes in frames).