Application of Protocols Devised to Study Bi(III) Complex Formation by Voltammetry: The Bi(III)-Picolinic Acid System

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Supporting Information

1) Description of selected symbols

E_j Diffusion junction potential

$E_{1/2}(M)$ Half-wave potential of the metal ion

$E(M)$ Reduction potential of the free or uncomplexed metal ion (also referred to as the free metal ion potential)

$E(M_{comp})$ Reduction potential of the complexed metal ion

$E_c(M)$ Conditional free metal ion potential

ΔE Shift in potential due to complex formation: $\Delta E = E(M) - E(M_{comp})$

$\Delta E(M)$ Difference in the free metal ion potentials for Bi(III) and Tl(I):
            $\Delta E(M) = E(Bi) - E(Tl)$

$\Delta E_c(M)$ Difference in the conditional and true free metal ion potentials for Bi(III) and Tl(I) respectively: $\Delta E_c(M) = E_c(Bi) - E(Tl)$
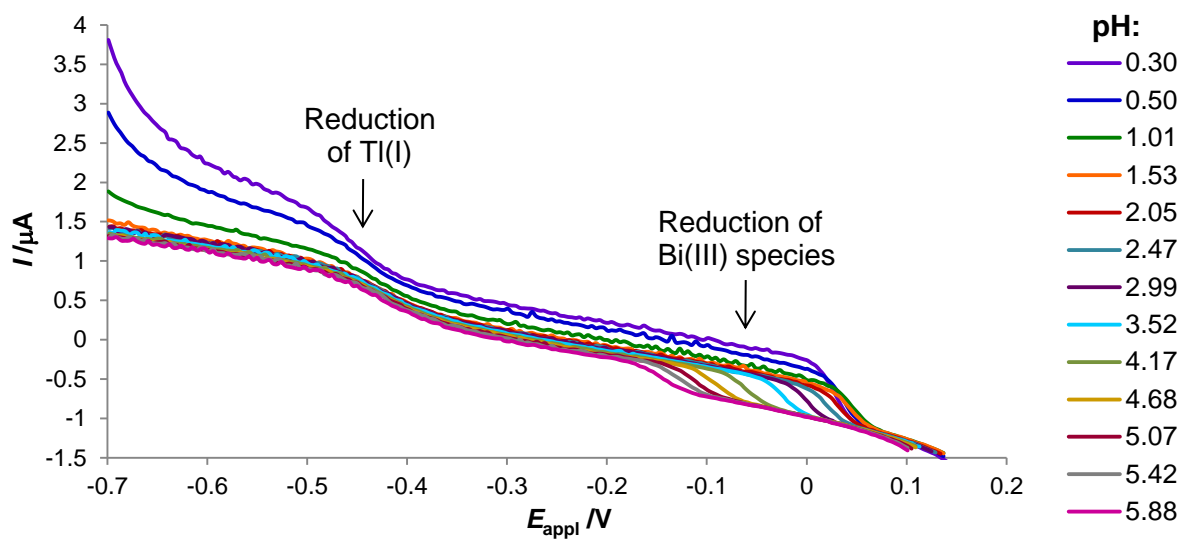
2) Information from polarographic-pH titrations

Figure S1. Selected polarograms from a polarographic-pH titration with $[PA_T]:[Bi_T] = 197$ (where initial concentrations were $[Bi(III)] = 1.0 \times 10^{-5}$ M and $[Tl(I)] = 2.0 \times 10^{-5}$ M.)

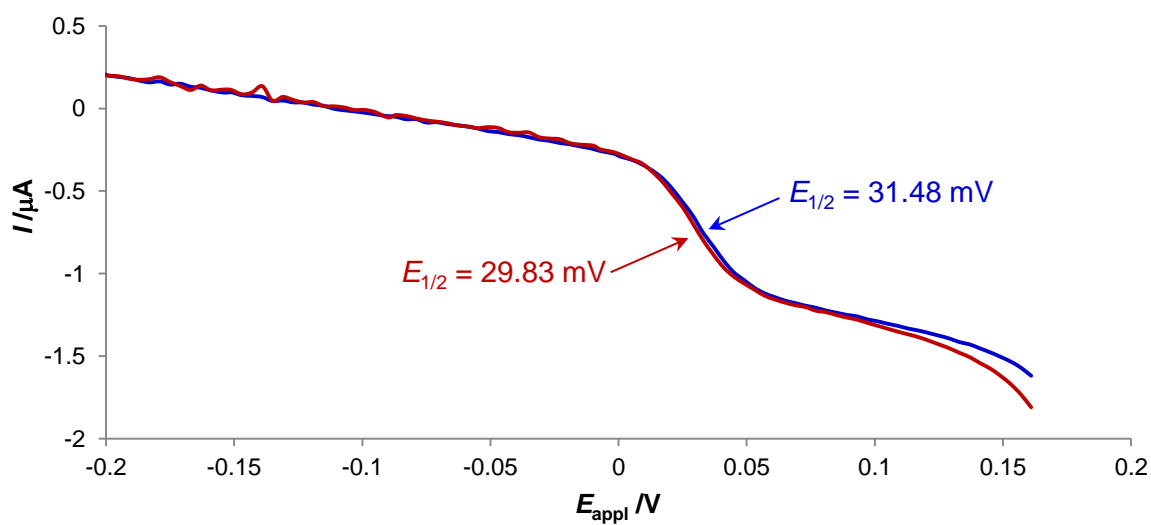**Figure S2.** Polarograms at pH 0.30 before (blue) and after (red) the addition of PA (where $[Bi(III)] = 1 \times 10^{-5}$ M and $[PA_T]:[Bi_T] = 197$. The $E_{1/2}$ values indicate a shift of 1.65 mV.
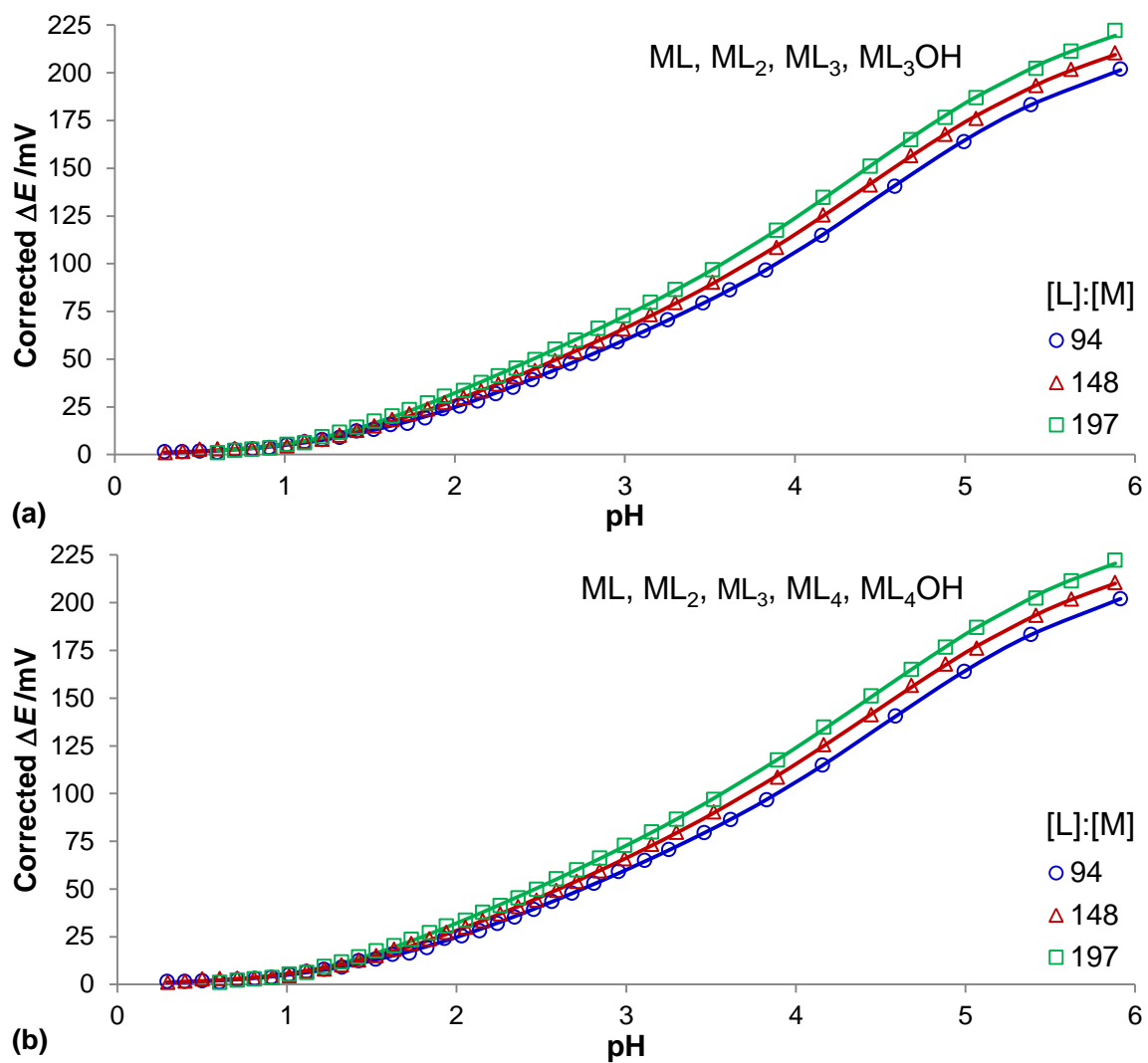
Figure S3. The ECFCs (points) and CCFCs (lines) at the indicated $[PA_T]:[Bi_T]$ for the two possible species models as determined using the 3D-CFC software.

Table S1. Log β values at 25 $^{\circ}$C for the proposed species models at ionic strength $0.25 - 0.5$ M (K,H)NO$_3$, as well as the overall fit of the CFCs as determined using the 3D-CFC software.

| [L]:[M]	94	148	197	Average
(a) Species Model 1				
ML	7.08 ± 0.08	7.01 ± 0.08	6.73 ± 0.13	6.94 ± 0.19
ML$_2$	13.98 ± 0.03	13.87 ± 0.03	13.94 ± 0.02	13.93 ± 0.06
ML$_3$	18.49 ± 0.13	18.55 ± 0.07	18.60 ± 0.07	18.55 ± 0.06
ML$_3$OH	28.26 ± 0.03	28.12 ± 0.03	28.25 ± 0.02	28.21 ± 0.08
Overall fit	0.31	0.41	0.64	
(b) Species Model 2				
ML	7.09 ± 0.08	7.03 ± 0.07	6.78 ± 0.12	6.97 ± 0.16
ML$_2$	13.97 ± 0.03	13.86 ± 0.03	13.92 ± 0.03	13.92 ± 0.06
ML$_3$	18.58 ± 0.14	18.62 ± 0.08	18.71 ± 0.07	18.64 ± 0.07
ML$_4$	22.97 ± 0.12	22.61 ± 0.10	22.54 ± 0.10	22.71 ± 0.23
ML$_4$OH	31.67 ± 0.06	31.33 ± 0.05	31.36 ± 0.04	31.45 ± 0.19
Overall fit	0.29	0.37	0.51	

3) **Published structure**
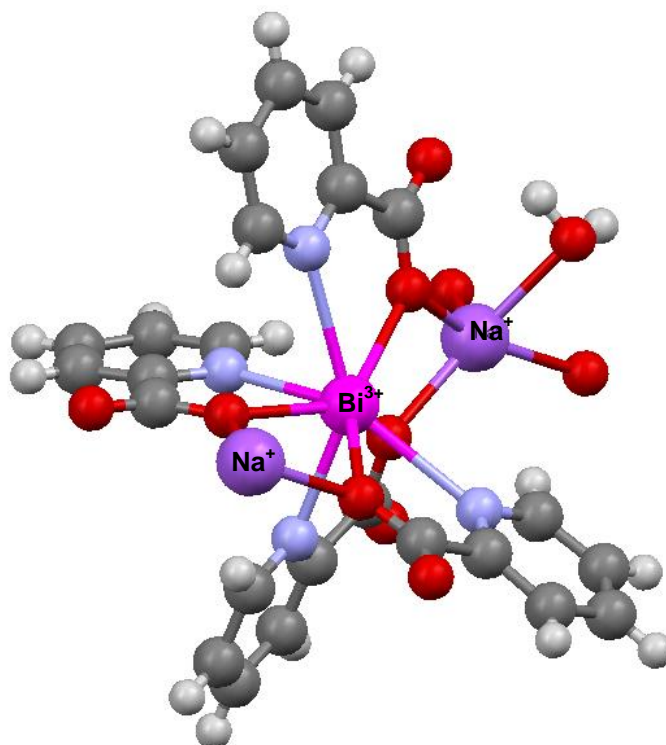
Figure S4. Structure of the Bi(III)-PA complex showing a BiL$_4$ arrangement[1] drawn using Mercury software.[2]

1) Allen, F.H. The Cambridge Structural Database: A Quarter of a Million Crystal Structures and Rising, *Acta Cryst. B* **2002**, *58*, 380-388. Cambridge Structural database Version 5.34, November 2012 update.
2) Macrae, C.F.; Edgington, P.R.; McCabe, P.; Pidcock, E.; Shields, G.P.; Taylor, R.; Towler, M.; van de Streek, J. Mercury: Visualization and Analysis of Crystal Structures. *J. Appl. Cryst.* **2006**, *39*, 453-457. Mercury, version 3.7.
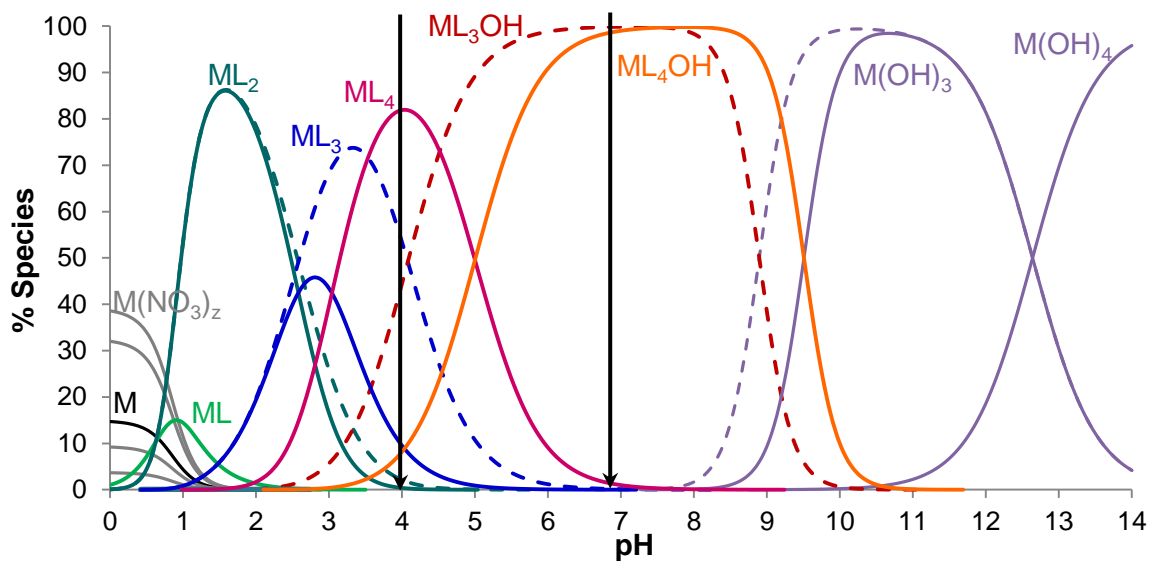
4) Information regarding ESI-MS studies

Figure S5. Species distribution diagrams are compared for aqueous solutions of Bi(III)-PA for species models including ML_3OH (dotted lines) or ML_4 and ML_4OH (solid lines) using log β values in Table 2 and with $[Bi(III)] = 1 \times 10^{-4}$ M and $[PA_T]:[Bi_T]_T = 100$. Solutions at pH 4.0 and 6.9 were analyzed by ESI-MS to elucidate the most probable species model.
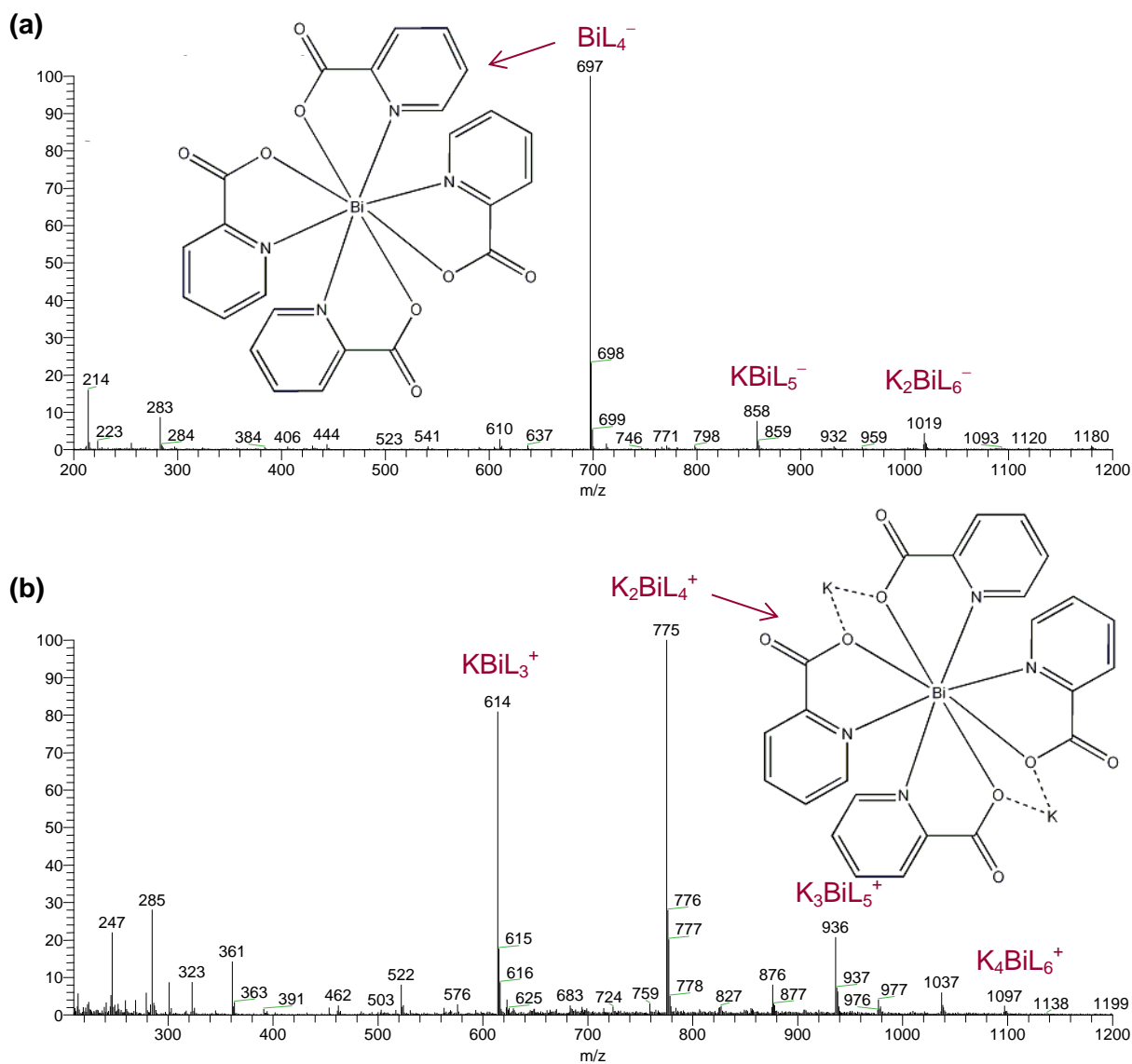
Figure S6. Mass spectra for (a) negative and (b) positive ions for the solution at pH 4.0 containing 10^{-4} M Bi(III) and 10^{-2} M PA in 0.5 M NO_3^-. In the assignment of peaks, only the mass-charge ratio (m/z) of the most abundant isotope is quoted. For example, the BiL_4^- species would produce relative abundances of 100.0% at m/z of 697, 26.4% at m/z of 698 and 5.3% at m/z of 699 (as determined from ChemDraw[1]).

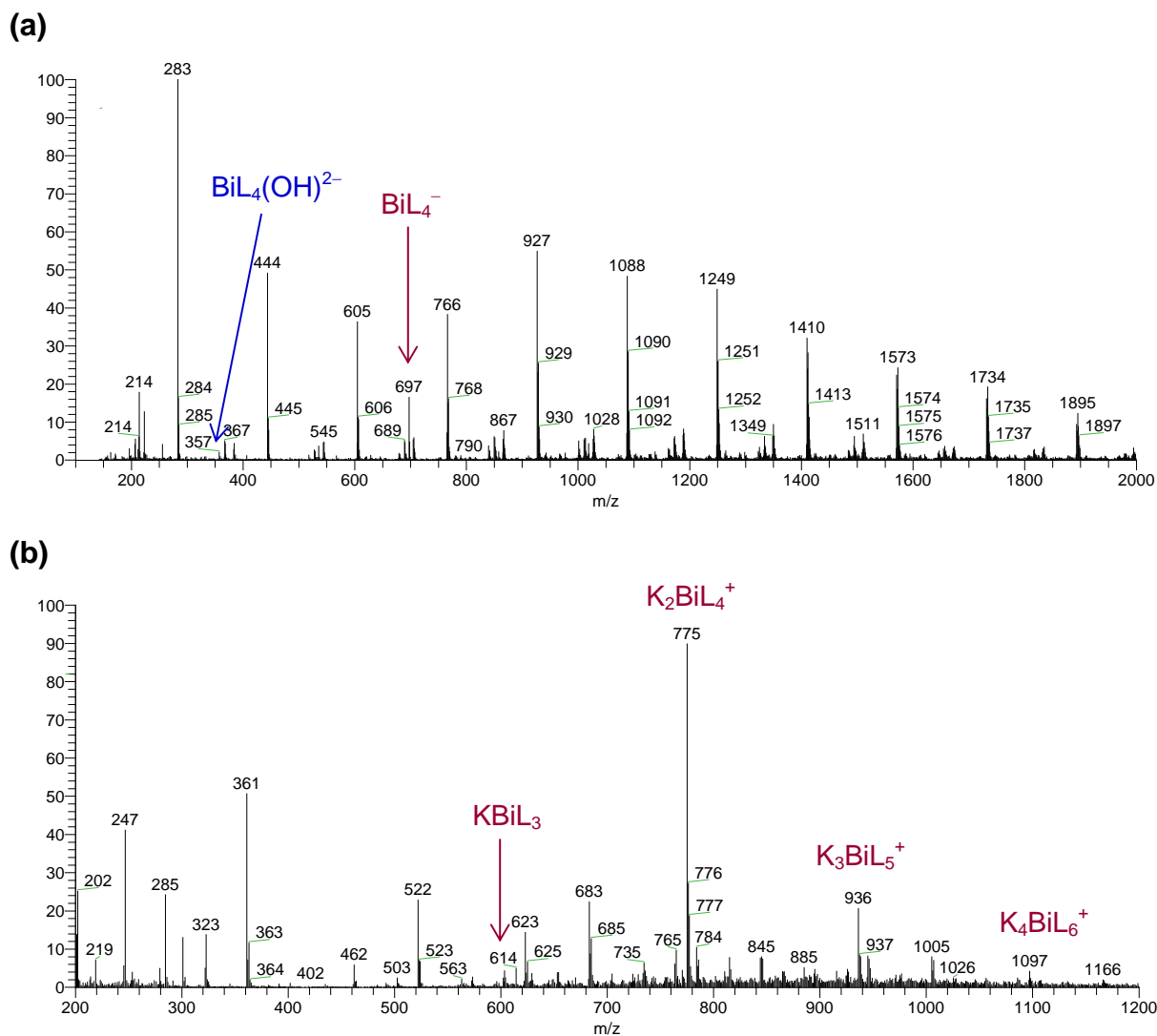1)   ChemDraw Ultra 8.0, CambridgeSoft Corporation, Cambrigde, USA, 2003

Figure S7. Mass spectra for (a) negative and (b) positive ions for the solution at pH 6.9 containing 10^{-4} M Bi(III) and 10^{-2} M PA in 0.5 M NO_3^-.

Table S2. Assignment of the mass spectra peaks (Figures S5 and S6) for positive and negative ions of species not containing Bi(III). Solutions analysed contained 10^{-4} M Bi(III) and 10^{-2} M PA in 0.5 M NO_3^- adjusted to (a) pH 4.0 and (b) pH 6.9.

(a) pH 4.0

m/z (+ve)	Assignment (+ve)	m/z (−ve)	Assignment (−ve)
247	$H_3L_2^+$	214	$KL(OH)(H_2O)_2^-$
285	$H_2KL_2^+$	283	KL_2^-
323	$HK_2L_2^+$		
361	$K_3L_2^+$		
522	$K_4L_3^+$		

(b) pH 6.9

m/z (+ve)	Assignment (+ve)	m/z (−ve)	Assignment (−ve)
247	$H_3L_2^+$	214	$KL(OH)(H_2O)_2^-$
285	$H_2KL_2^+$	283	KL_2^-
323	$HK_2L_2^+$	444	$K_2L_3^-$
361	$K_3L_2^+$	605	$K_3L_4^-$
522	$K_4L_3^+$	766	$K_4L_5^-$
623	$K_5L_3(NO_3)^+$	927	$K_5L_6^-$
683	$K_5L_4^+$	1088	$K_6L_7^-$
784	$K_6L_4(NO_3)^+$	1249	$K_7L_8^-$
845 (844)*	$K_6L_5^+$	1410	$K_8L_9^-$
1005	$K_7L_6^+$	1573 (1571)*	$K_9L_{10}^-$
		1734 (1732)*	$K_{10}L_{11}^-$
		1895 (1893)*	$K_{11}L_{12}^-$

* Actual values calculated are given in brackets. In the mass spectrum it was noted that the most abundant value was quoted, but there was a peak just before this which probably corresponded to the m/z value in brackets.

5) Derivation of MBEs for use in a spreadsheet

In general, there are three MBEs that need to be considered for aqueous metal-ligand systems, namely:

$$[M_T] = [M] + \sum_p \sum_q \sum_r p \, \beta_{pqr}[M]^p[L]^q[H]^r \qquad\qquad (S1)$$

$$[L_T] = [L] + \sum_p \sum_q \sum_r q \, \beta_{pqr}[M]^p[L]^q[H]^r \qquad\qquad (S2)$$

$$[H_T] = [H] + \sum_p \sum_q \sum_r r \, \beta_{pqr}[M]^p[L]^q[H]^r \qquad\qquad (S3)$$

where $r < 0$ indicates [OH] and [M], [L] and [H] or [OH] signify the concentrations of the uncomplexed components. The values of $[M_T]$ and $[L_T]$ are known since specific concentrations are added and their concentrations can be calculated throughout the titration experiment by accounting for dilution. In order to calculate the stability constants (β_{pqr}) using polarographic data, the value of [M] must be determined (as indicated in eq 1), but in order to do so both [L] and [H] (or [OH]) must be known. The value of [H] (or [OH]) is calculated using the pH values obtained from the GE measurement and calibration. The values of [M] and [L] have to be determined simultaneously and both these values are dependent on the stability constants β_{pqr}. Using a non-linear least squares method, the values of β_{pqr} (for the types of solution species $M_pL_qH_r$ predicted) need to be initially estimated and then refined such that the sum of squares of errors between the calculated function (CCFC) and the experimental data (ECFC) is minimized.

Certain assumptions can be made to simplify the calculation of [M], as was done by Foti *et al.*[1] Firstly, when voltammetric methods are employed to study complex formation a large $[L_T]:[M_T]$ is used (generally >100) to ensure that the solution close to the electrode surface is representative of the bulk solution during measurement. It can therefore be assumed that the concentration of ligand involved in complex formation is negligible compared to $[L_T]$ and thus only the extent of protonation of the ligand needs to be considered, i.e.:

$$[L_T] = [L] + \sum_r \beta_{01r}[L][H]^r \qquad\qquad (S4)$$

$$[L] = [L_T] \Big/ \left(1 + \sum_r \beta_{01r}[H]^r\right) \qquad\qquad (S5)$$

Secondly, for very low $[M_T]$ it can be assumed that no polynuclear species are formed (i.e. $p = 1$ or 0). The question is whether the latter assumption is valid in the case of Bi(III) which readily for forms polynuclear hydrolysis species. In this work $[Bi_T]$ was initially 1×10^{-5} M and was approximately halved during the pH titration experiment. Figure S7 shows the SDD

for the hydrolysis species at these concentrations. At the initial Bi(III) concentration the only polynuclear species present is $Bi_9(OH)_{22}^{5+}$ (25% of $[Bi_T]$) which forms around pH 4 – 6. To reach a pH of 4 by addition of 0.5 M KOH in the titration experiment, the Bi(III) concentration is reduced to about 5×10^{-6} M where the concentration of $Bi_9(OH)_{22}^{5+}$ is no longer significant. Additionally, in the presence of a ligand such as picolinic acid, polynuclear species should be non-existent. The simplified MBE can thus be written as:

$$[M_T] = [M] + \sum_q \sum_r \beta_{1qr}[M][L]^q[H]^r \tag{S6}$$

$$[M] = {[M_T]} \Big/ {\left(1 + \sum_q \sum_r \beta_{1qr}[L]^q[H]^r \right)} \tag{S7}$$
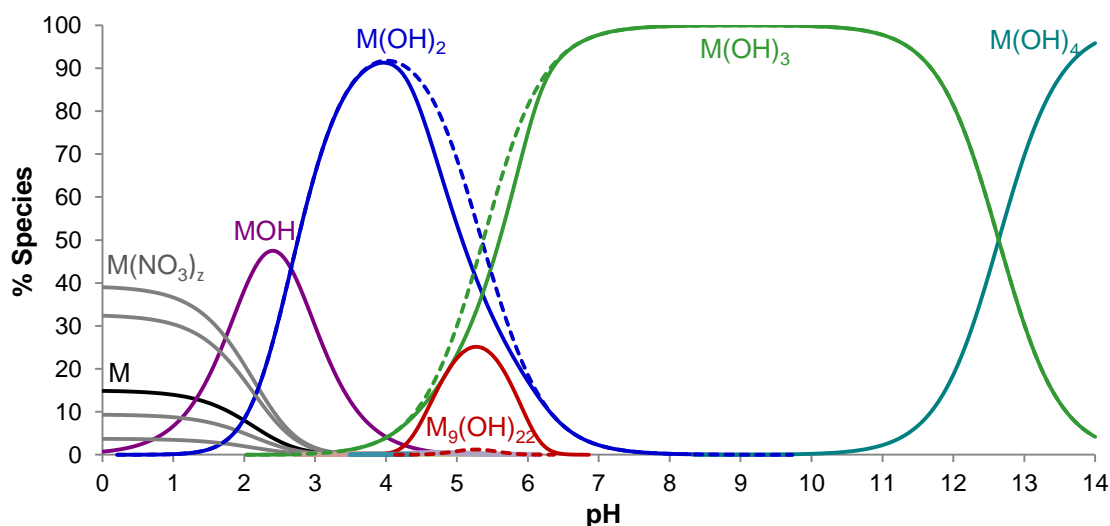

Figure S8. SDD showing hydrolysis species for $[Bi_T]$ of 1×10^{-5} M (solid lines) and 5×10^{-4} M (dotted line).

To incorporate competition between the ligand and nitrate (represented as X), the stability constants of the Bi(III)-nitrates (indicated as β'_{1z} where z = 1 – 4) were kept constant as given in Table 1 and it was assumed that nitrate was fully deprotonated throughout the titration pH range (a valid assumption since $pK_a = -1.64$ for HNO_3)[2]. Also, since there is 50 000 times more nitrate in solution than Bi(III), it was assumed that that $\sum[MX_z] \ll [X_T]$ and thus $[X_T] = [X]$. The MBE used in calculations was:

$$[M] = {[M_T]} \Big/ {\left(1 + \sum_q \sum_r \beta_{1qr}[L]^q[H]^r + \sum_z \beta'_{1z}[X]^z \right)} \tag{S8}$$

The nitrate concentration was set equal to that for HNO_3 (a standardized solution) and small discrepancies introduced from the metal ion stock solutions were ignored (only a few μL of stock solution is added to 25 mL background electrolyte).

An Excel spreadsheet was thus constructed to calculate [H] and [OH] from the pH determinations, [X] by accounting for dilution of nitrate, [L] by using MBE S5and [M] by using MBE S8 with estimated β_{1qr} values (β_{10r} and β'_{1t} values were kept fixed), for each step in the titration. [L_T] and [M_T] values were also calculated by accounting for dilution. The ECFC and CCFC were then calculated at each pH step using the left- and right-hand sides of eq. 1, respectively. The square of difference between the ECFC and CCFC was then calculated and summed. The resulting sum of squares of errors was then minimized using the GRG nonlinear solving method in Excel Solver by refining the β_{1qr} values.

1) Foti, C.; Lando, G.; Millero, F.J.; Samartano, S. Experimental Study and Modelling of Inorganic Cd^{2+} Speciation in Natural Waters. *Envir. Chem.* **2011**, *8*, 320-331.
2) Housecroft, C.E.; Sharpe, A.G. Inorganic Chemistry (2nd ed.), Prentice Hall, 2004

6) Information from polarographic-pH titrations when including the Bi(III)-nitrates in the species model

Table S3. Log β values (and the overall fit of the CFCs) calculated using (a) the spreadsheet where the Bi(III)-nitrates are included as competing species and (b) the 3D-CFC software with a sliding $E_c(M)$. The values are applicable at 25 °C and ionic strength $0.25 - 0.5$ M (K,H)NO$_3$.

(a) Use spreadsheet and account for MX$_z$ in species model			
[L]:[M]	**94**	**148**	**197**	**Average**
ML	7.83	7.78	7.70	7.77 ± 0.07
ML$_2$	13.88	13.82	13.97	13.89 ± 0.07
ML$_3$	18.61	18.60	18.61	18.606 ± 0.005
ML$_4$	22.87	22.57	22.57	22.67 ± 0.17
ML$_4$OH	31.60	31.28	31.31	31.40 ± 0.18
Overall fit	1.26	1.15	1.38	

(b) Use 3D-CFC software with a sliding $E_c(M)$			
[L]:[M]	**94**	**148**	**197**	**Average**
ML	7.61 ± 0.03 (7.61)	7.52 ± 0.03 (7.52)	7.37 ± 0.04 (7.37)	7.50 ± 0.12 (7.50 ± 0.12)
ML$_2$	13.99 ± 0.04 (13.97)	13.92 ± 0.03 (13.91)	14.04 ± 0.03 (14.03)	13.98 ± 0.06 (13.97 ± 0.06)
ML$_3$	18.47 ± 0.19 (18.44)	18.51 ± 0.11 (18.49)	18.54 ± 0.11 (18.52)	18.51 ± 0.04 (18.48 ± 0.04)
ML$_4$	23.01 ± 0.10 (22.94)	22.68 ± 0.09 (22.63)	22.66 ± 0.08 (22.62)	22.78 ± 0.20 (22.73 ± 0.18)
ML$_4$OH	31.66 ± 0.06 (31.58)	31.31 ± 0.05 (31.26)	31.34 ± 0.05 (31.30)	31.44 ± 0.19 (31.38 ± 0.18)
Overall fit	0.30 (0.59)	0.34 (0.62)	0.60 (0.82)	

Values in brackets for (b) were obtained when using the same data but the log β values where calculated using the spreadsheet simply to check the validity of calculations in the spreadsheet.
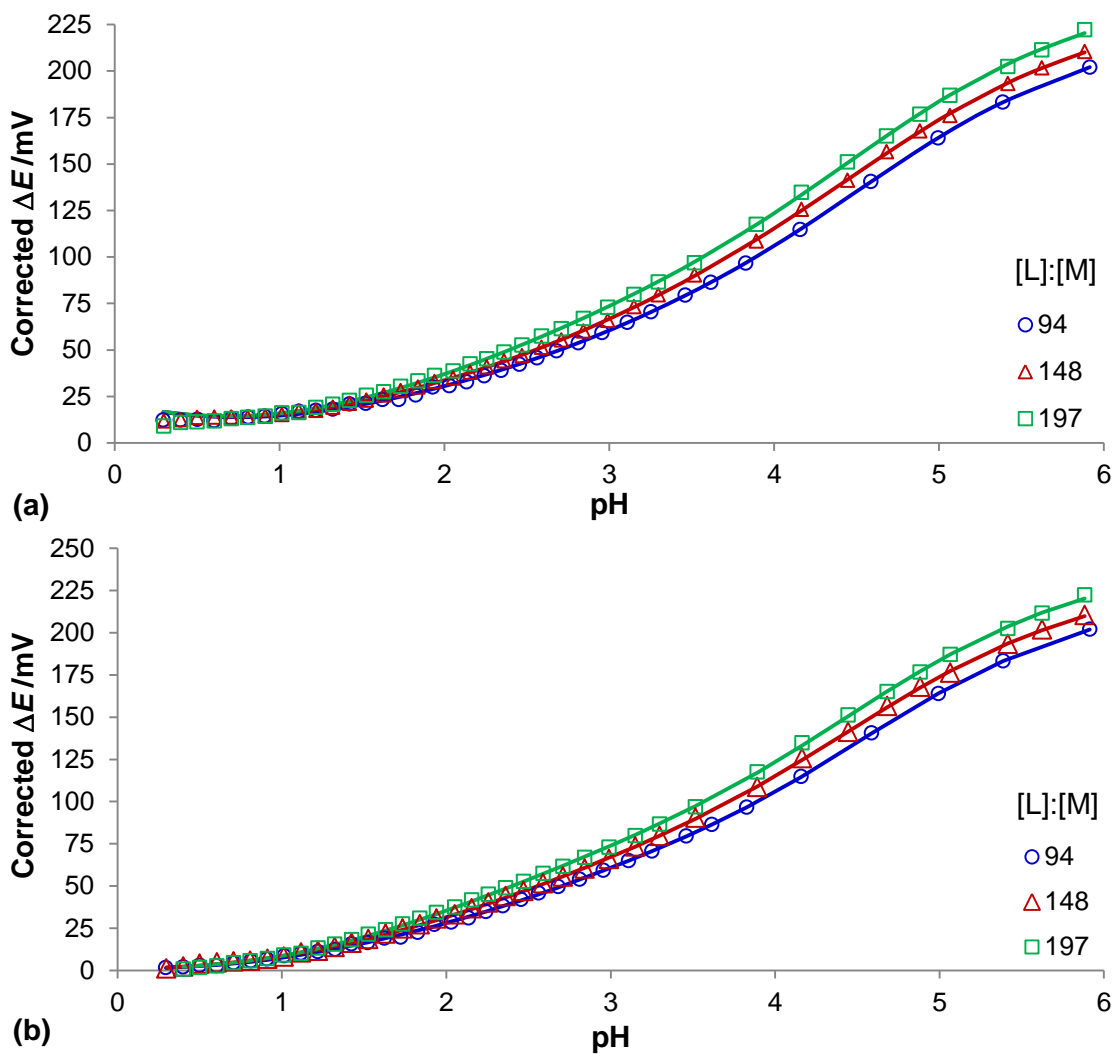
Figure S9. The ECFCs (points) and CCFCs (lines) at the indicated $[PA_T]:[Bi_T]$ calculated using (a) the spreadsheet where the Bi(III) nitrates are included as competing species and (b) the 3D-CFC software with a sliding $E_c(M)$.

7)   Comparison of stability constants for various metal ion-picolinic acid complexes

Table S4. Comparison of selected log β values for the complexation of various metal ions by picolinic acid as presented in the NIST database[1] (except for that of Bi(III) which was determined in this work).

M	log β(ML)	log β(ML$_2$)	log β(ML$_3$)	log β(ML$_4$)	μ /M	T /°C
Al(III)	4.51	8.38	12.0		0.5	25
Mn(II)	3.57	6.32	8.1		0.1	20
Fe(II)	4.9	9.00	12.30		0.1	20
Co(II)	5.74	10.44	14.09		0.1	20
Ni(II)	6.72	12.44	17.07		0.1	25
Cu(II)	7.87	14.78			0.1	25
Zn(II)	5.23	9.56	12.9		0.1	25
Cd(II)	4.35	8.00	10.79		0.1	25
In(III)	5.81	11.56	15.57		0.1	25
Hg(II)	7.70	15.55			0.1	20
Pb(II)	4.49	7.58	9.59		0.5	25
Bi(III)	7.78	12.89	18.60	22.7	0.5	25
La(III)	3.19	5.85	8.2	10.0	0.5	25

1)   Martell, A.E.; Smith, R.M. Motekaitis, R.J. NIST Standard Reference Database 46 Version 8.0. NIST Critically Selected Stability Constants of Metal Complexes Database, Gaithersburg, USA, 2004.