Cu²⁺ and AMP Complexation of Enlarged Tripodal Polyamines

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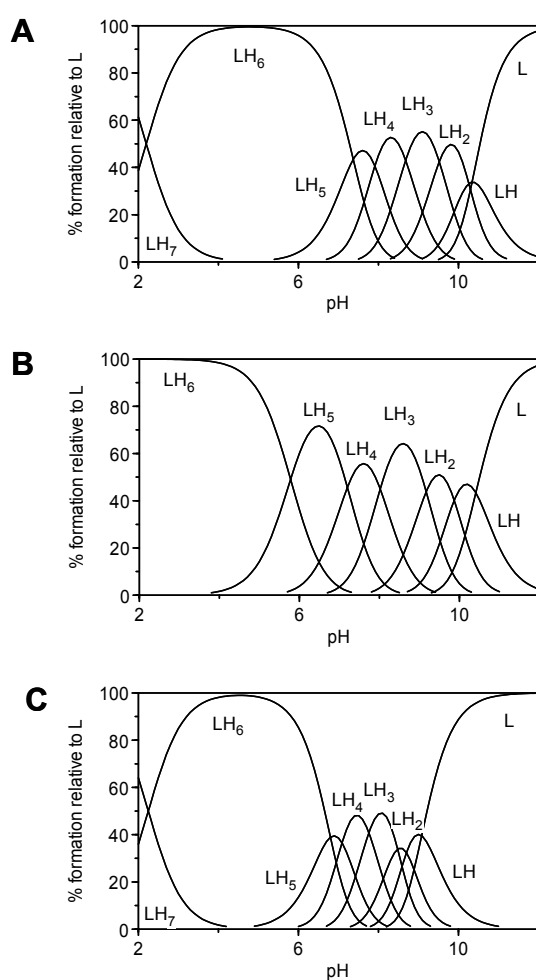
Fig. S1. Distributions diagrams for the systems (A) H⁺-**TAL**; (B)) H⁺-**ATAL**; (C) H⁺-**N3TAL**.

Table S1 Observed chemical shifts for the interaction of AMP with the tripodals ligands **TAL, ATAL**

[AMP]/[L]	TAL	ATAL
0,5	3,14	3,72
0.75	3,11	3,73
1	2.41	3,66
1.25	2,41	
1.5	2,29	3,33
1.75	2,22	3,24
2	2,11	3,12
2.25	1,91	
2.5	1,92	3,02
2.75	1,85	3
3	1,77	2,77
3,5	1,67	
4	2,3	
4,5	2,17	2,67
5	2,13	

Table S2 Logarithms of the equilibrium constants for the interaction of AMP (AMP ≡ A) with the tripodal polyamines **TAL**, **ATAL** and **N3TAL** determined at 298.0 ±0.1 K in 0.15 mol·dm^{-3} NaCl.

Reaction	TAL	ATAL	N3TAL
A+ L ⇄ AL [a]	4.76(5)	6.41(6)	5.3(1)[b]
A + H +L ⇄ HAL	15.51(5)	16.81(7)	15.36(9)
A + 2H + L ⇄ H$_2$AL	25.62(5)	26.84(6)	23.8(1)
A + 3H + L ⇄ H$_3$AL	35.34(5)	36.08(6)	32.56(8)
A + 4H + L ⇄ H$_4$AL	44.07(5)	44.27(6)	40.17(9)
A + 5H + L ⇄ H$_5$AL	52.09(5)	51.82(7)	47.53(8)
A + 6H + L ⇄ H$_6$AL	59.44(4)	58.10(4)	54.14(8)
A + 7H + L ⇄ H$_7$AL	64.2(1)		59.15(8)
2A+5H+L ⇄ H$_5$A$_2$L	54.8(1)		
2A+6H+L ⇄ H$_6$A$_2$L	62.33(9)		
2A+7H+L ⇄ H$_7$A$_2$L	68.80(8)		
2A+8H+L ⇄ H$_8$A$_2$L	74.14(5)	71.1(1)	
3A+5H+L ⇄ H$_5$A$_3$L	58.54(5)		
3A+6H+L ⇄ H$_6$A$_3$L	66.17(5)	64.97(8)	
3A+7H+L ⇄ H$_7$A$_3$L	72.71(5)		
3A+8H+L ⇄ H$_8$A$_3$L	78.79(5)		
3A+9H+L ⇄ H$_9$A$_3$L	83.91(4)		

[a] Charges omitted for clarity. [b] Numbers in parentheses are standard deviations in the last significant figure

Table S3. ^{1}H NMR hyperfine-shifted resonances and temperature dependence of Cu_2**TAL**, Cu_2**TAL** - AMP complexes in D_2O at 25 °C and pH 8.

Complex	Signal	δ(ppm)	N° of protons	Assign.	Temperature dependence	T_1 (ms)	$\Delta\nu_{1/2}$ (Hz)	T_2 (ms)[a]
Cu_2**TAL**	a	3.6	6	βCH_2	Anti-Curie	3.7	150	2.1
	b	2.4			Anti-Curie	<1	b	b
	B	1.2	24	αCH_2	Anti-Curie	b	b	b
	c	0.28			Anti-Curie	<1	341	0.93
	d	-9.3			Curie	<1	1624	0.20
Cu_2**TAL**-AMP	a'	3.6	6	βCH_2	Anti-Curie	2.5	195	1.6
	b'	2.5			Anti-Curie	<1	b	b
	c'	0.27	24	αCH_2	Anti-Curie	<1	361	0.88
	d'	-9.2			Curie	<1	1131	0.28
	e'	8.7	2x2	γCH_2-AMP	Anti-Curie	11.2	78	4.1
	g'	6.1	2x2	$H_{2,8}CH$-AMP[c]	Anti-Curie	48.7	18	17.7
	f'	8.2			Anti-Curie	45.4	30	10.6
	h'	4.4	4x2	$\delta-\sigma CH$-AMP[c]	Anti-Curie	36.8	b	b
	i'	4.3			Anti-Curie	35.3	b	b
	j'	3.9			Anti-Curie	21.9	24	13.3

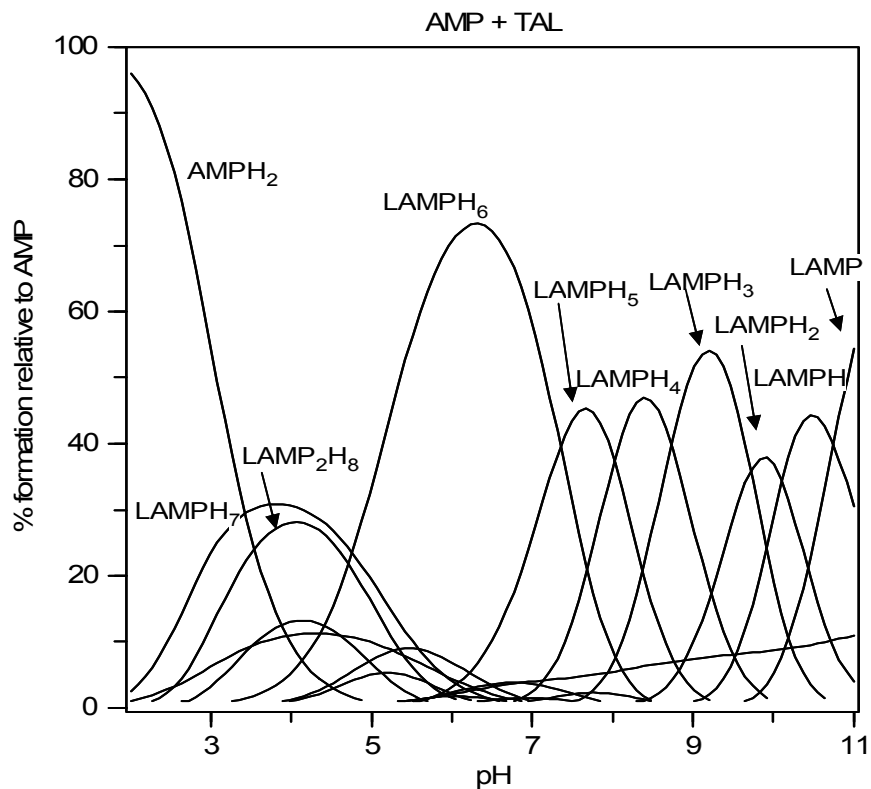[a] Measured from the line width at half-height. [b] Overlap prevents measurement of this value. [c] Tentative assignments.

Fig. S2 Distribution Diagrams for the system **TAL**-AMP. [**TAL**] = $1 \cdot 10^{-3}$ mol·dm^{-3}, [AMP] = $1 \cdot 10^{-3}$ mol·dm^{-3}.
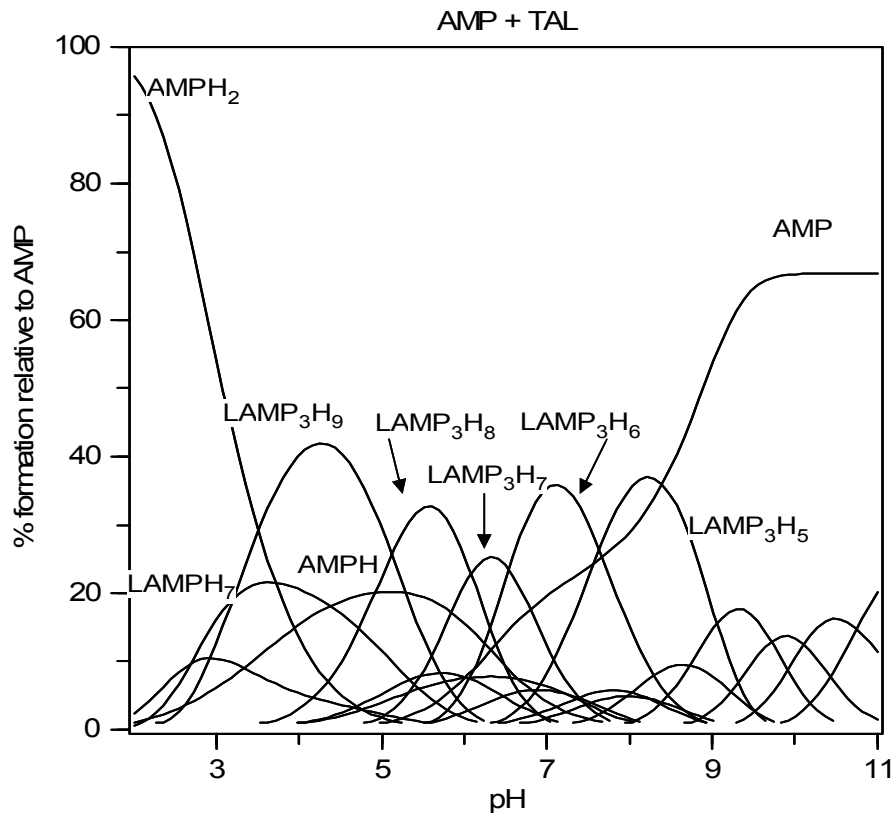

Fig. S3 Distribution Diagrams for the system **TAL**-AMP. [**TAL**] = $1 \cdot 10^{-3}$ mol·dm^{-3}, [AMP] = $3 \cdot 10^{-3}$ mol·dm^{-3}.
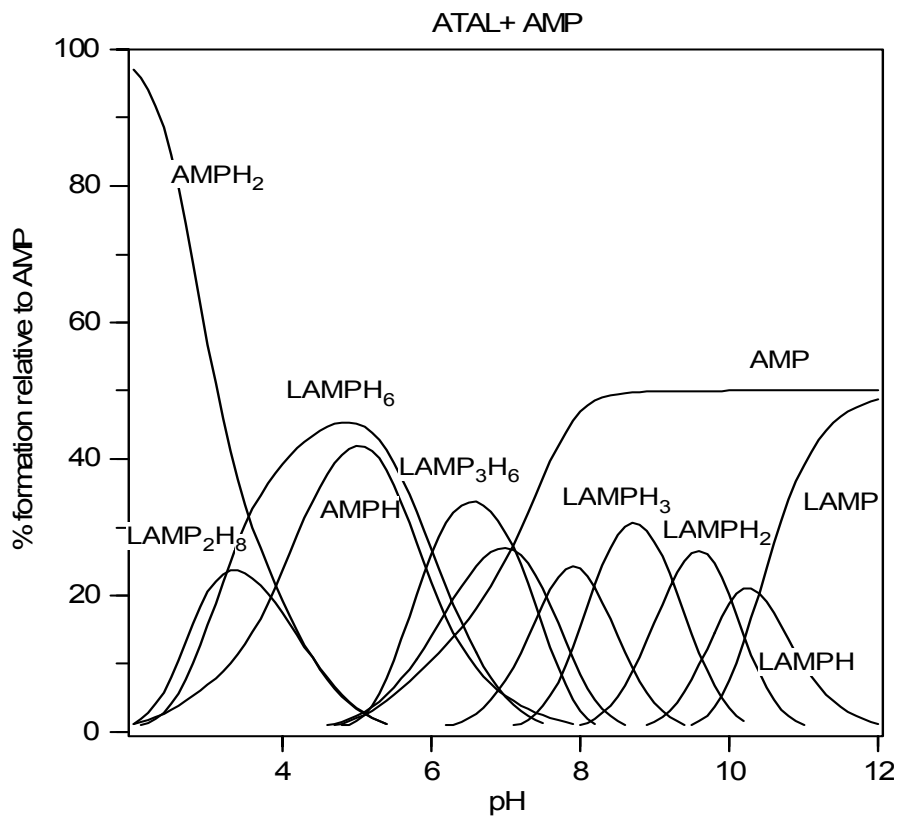
Fig. S4 Distribution Diagrams for the system **ATAL**-AMP. [**ATAL**] = $1 \cdot 10^{-3}$ mol·dm^{-3}, [AMP] = $2 \cdot 10^{-3}$ mol·dm^{-3}.
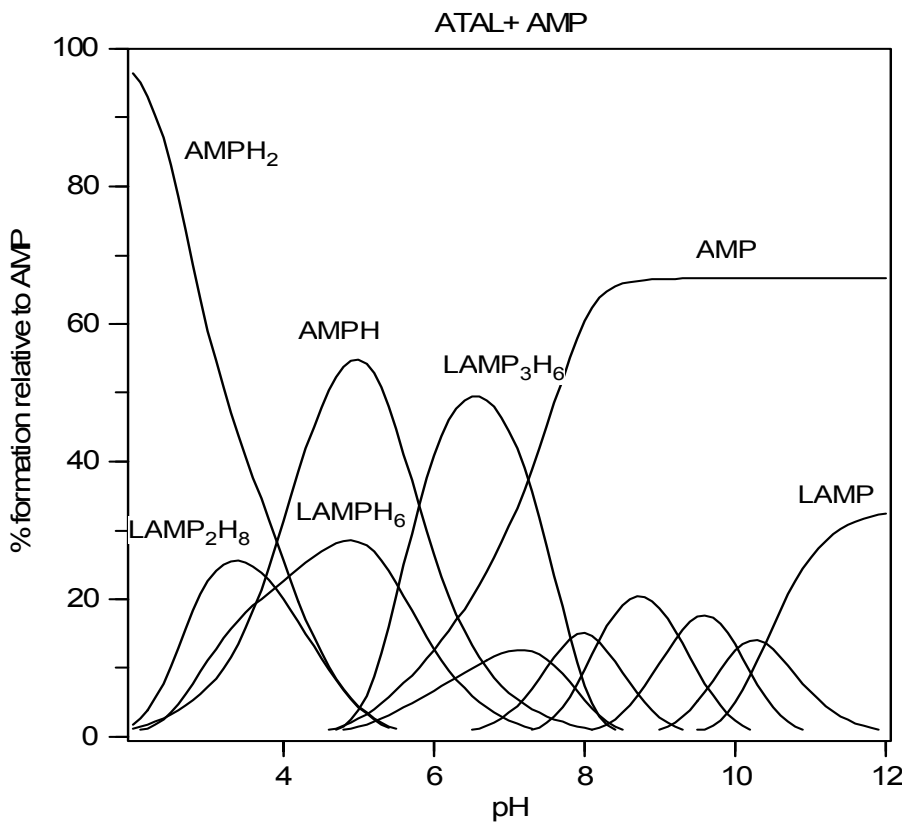
Fig. S5 Distribution Diagrams for the system **ATAL**-AMP. [**ATAL**] = $1 \cdot 10^{-3}$ mol·dm^{-3}, [AMP] = $3 \cdot 10^{-3}$ mol·dm^{-3}.
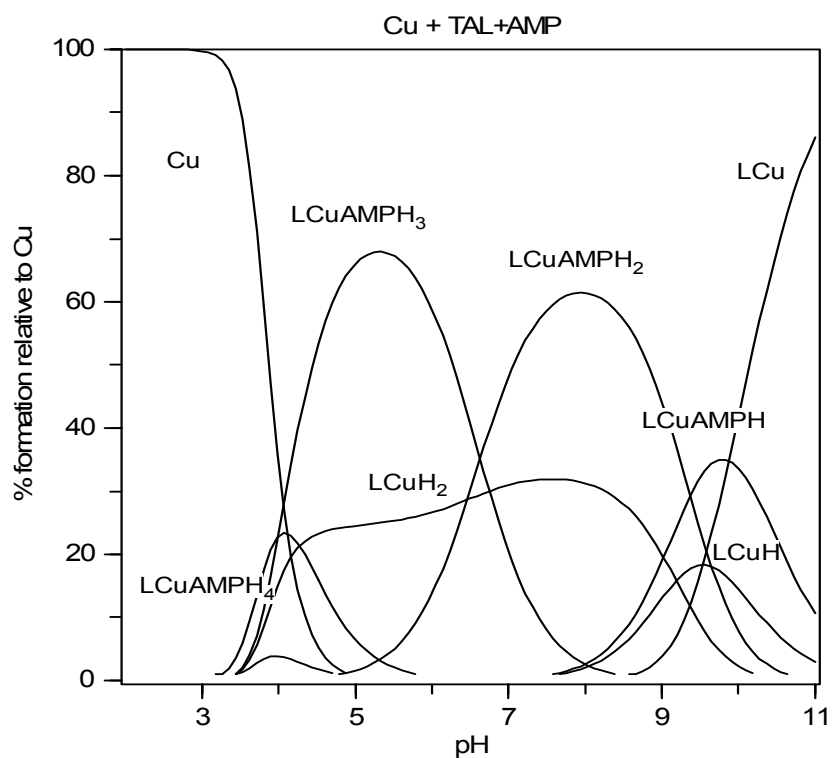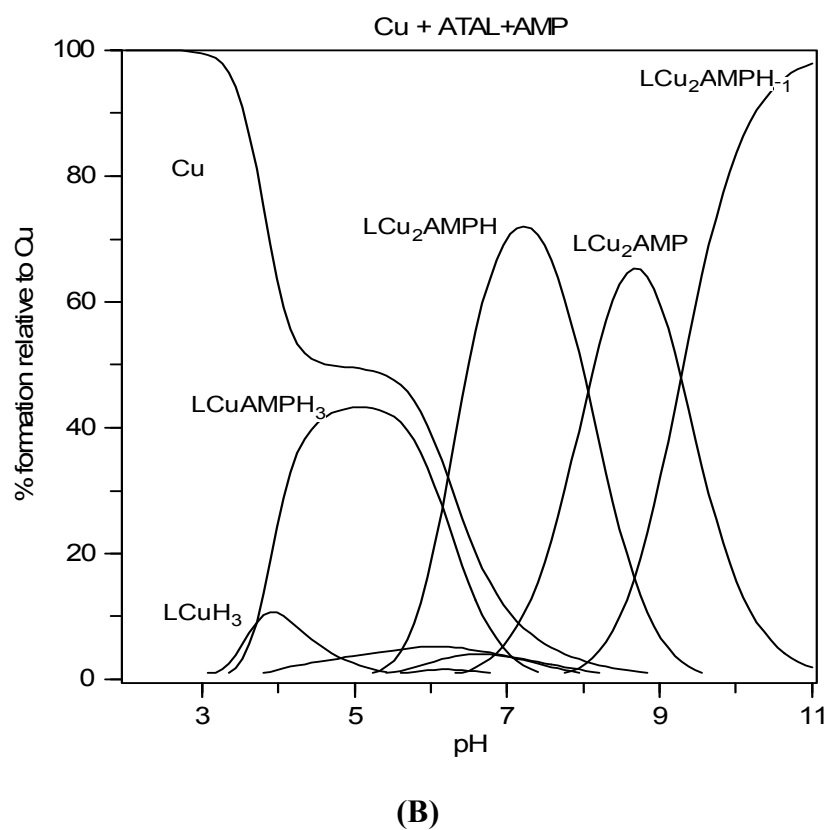
(A)

(B)
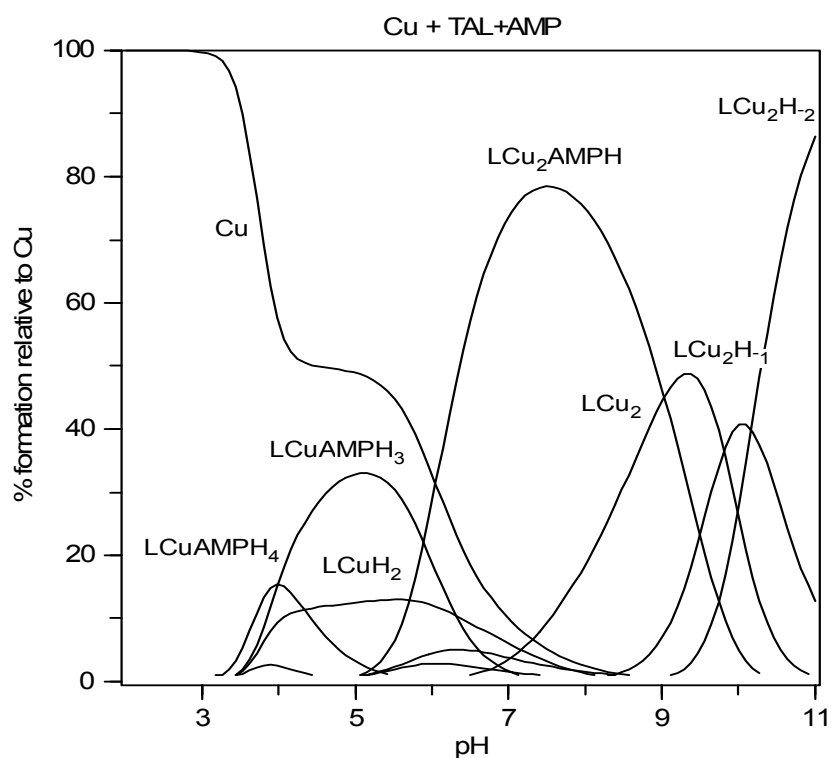
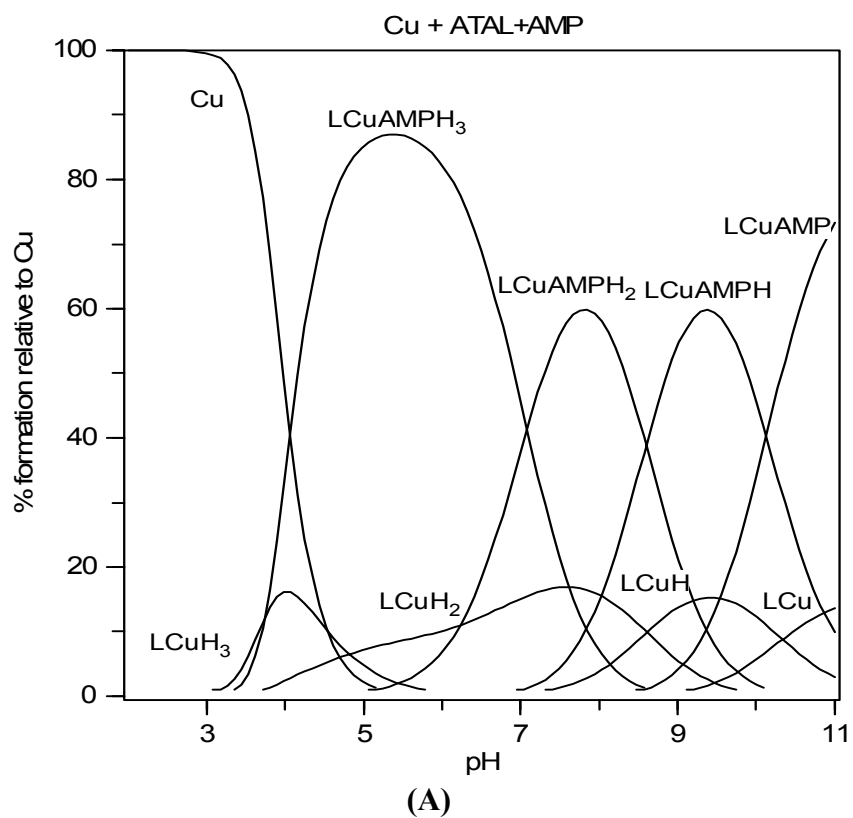**Fig. S6** Distribution Diagrams for the ternary system Cu^{2+}-**TAL**-AMP. (A) $[Cu^{2+}] = [\textbf{TAL}] = [AMP] = 1 \cdot 10^{-3}$ mol·dm^{-3}. (B) $[Cu^{2+}] = 2 \cdot 10^{-3}$ mol · dm^{-3}, $[\textbf{TAL}] = [AMP] = 1 \cdot 10^{-3}$ mol·dm^{-3}

(A)

(B)

Fig. S7 Distribution Diagrams for the ternary system Cu^{2+}-**ATAL**-AMP. (A) $[Cu^{2+}]$ = [**ATAL**] = [AMP] = $1 \cdot 10^{-3}$ mol·dm^{-3}. (B) $[Cu^{2+}]$ = $2 \cdot 10^{-3}$ mol·dm^{-3}, [**ATAL**] = [AMP] = $1 \cdot 10^{-3}$ mol·dm^{-3}.
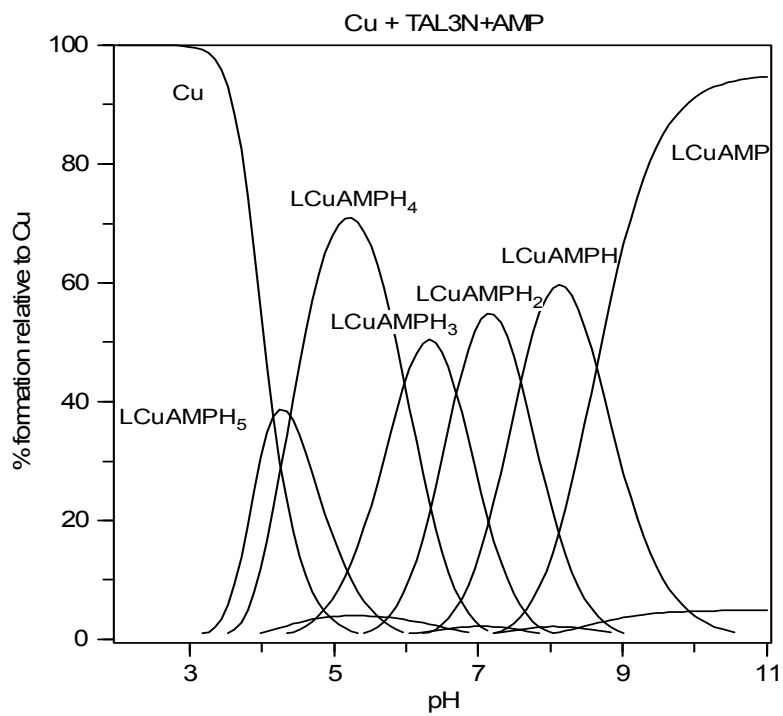
Fig. S8 Distribution Diagrams for the ternary system Cu^{2+}-**N3TAL**-AMP. $[Cu^{2+}]$ = [**N3TAL**] = [AMP] = $1 \cdot 10^{-3}$ mol·dm^{-3}.