Table ESI 1 Equilibrium constants used to model the solution speciation. L = maltolate.

Reaction	$^{*}\log\beta_i$ (I=0.6)	$\log\prod\gamma_i$ (I=0.6)	$\log\prod\gamma_i$ (I=1.5)	$\log\beta_i$ (I=1.5)
$HL \leftrightarrow H^+ + L^-$	-8.3810	-0.3226	-0.2529	-8.3113
$Al^{3+} + HL \leftrightarrow AlL^{2+} + H^+$	-0.1300	0.4653	0.0559	-0.5394
$Al^{3+} + 2HL \leftrightarrow AlL_2^+ + 2H^+$	-0.9560	0.6679	0.0088	-1.6151
$Al^{3+} + 3HL \leftrightarrow AlL_3 + 3H^+$	-2.6690	0.6079	-0.1412	-3.4181
$2Al^{3+}+2HL+2H_2O \leftrightarrow Al_2L_2(OH)_2^{2+} + 4\ H^+$	-7.2030	1.1932	0.2148	-8.1814
$Al^{3+} + H_2O \leftrightarrow Al(OH)^{2+} + H^+$	-5.5200	-1.8386	-0.7205	-4.4019
$Al^{3+} + 2H_2O \leftrightarrow Al(OH)_2^+ + 2H^+$	-11.300	0.7879	0.3088	-11.7791
$Al^{3+} + 3H_2O \leftrightarrow Al(OH)_3 + 3H^+$	-17.300	0.7879	0.3088	-17.7791
$Al^{3+} + 4H_2O \leftrightarrow Al(OH)_4^- + 4H^+$	-23.500	0.5253	0.2059	-23.8194
$13Al^{3+} +18H_2O \leftrightarrow Al_{13}^{7+} + 32H^+$	-105.50	4.7277	1.8536	-108.374

*Data from Hedlund and Öhman[9] combined with those compiled in Phillips et al.[13]

Table ESI 2: Aluminum and oxygen speciation in the Al(III)-maltolate complexes based on ^{27}Al NMR

Temp	Aluminum speciation				pH		Oxygen speciation*		
(°C)	Al^{3+}	$Al(L)^{2+}$	$Al(L)_2^{+}$	$Al(L)_3$	pH_{calc}	pH_{meas}	Al^{3+}	$Al(L)^{2+}$	$Al(L)_2^{+}$
32-68-4									
60	0.0425	0.3836	0.5147	0.0592	2.81	2.8	0.0905	0.5443	0.3652
50	0.0538	0.3788	0.4946	0.0728	2.87		0.1142	0.5359	0.3499
40	0.0535	0.3790	0.4938	0.0736	2.85		0.1136	0.5367	0.3496
20	0.0660	0.3842	0.4572	0.0926	3.09	3.1[a]	0.1391	0.5398	0.3212
10	0.0822	0.3847	0.4190	0.1141	3.66		0.1718	0.5362	0.2920
0	0.1194	0.3819	0.3132	0.1856	3.65		0.2496	0.5322	0.2182
32-66-1									
60	0.2118	0.5804	0.2078		1.89	1.78	0.3171	0.5792	0.1037
50	0.2292	0.5780	0.1928		1.95		0.3377	0.5677	0.0947
40	0.2385	0.5597	0.2018		1.95		0.3513	0.5496	0.0991
30	0.2478	0.5444	0.2078		1.96		0.3644	0.5337	0.1019
20	0.2701	0.5493	0.1807		2.06	1.88[a]	0.3878	0.5257	0.0865
10	0.2859	0.5450	0.1691		2.14		0.4052	0.5149	0.0799
0	0.2738	0.5950	0.1312		2.22		0.3834	0.5554	0.0612
32-66-5									
60	0.3434	0.5263	0.1303		1.35	1.40	0.4655	0.4756	0.0589
50	0.3734	0.5072	0.1194		1.37		0.4970	0.4500	0.0530
40	0.3986	0.4766	0.1248		1.38		0.5259	0.4192	0.0549
30	0.4433	0.4507	0.1063		1.41		0.5689	0.3856	0.0455
20	0.4702	0.4288	0.1010		1.43	1.45[a]	0.5954	0.3620	0.0426
10	0.5142	0.3999	0.0859		1.47		0.6353	0.3294	0.0354
0	0.5434	0.3629	0.0937		1.48		0.6655	0.2963	0.0382
32-66-2									
60	0.0088	0.2143	0.6394	0.1376	2.67	2.85	0.0240	0.3916	0.5843
50	0.0075	0.1964	0.6375	0.1586	2.85		0.0213	0.3732	0.6056
40	0.0136	0.2218	0.6216	0.1431	2.97		0.0369	0.4010	0.5620
30	0.0156	0.2292	0.6065	0.1487	2.97		0.0422	0.4123	0.5456
20	0.0182	0.2425	0.5811	0.1582	2.62	2.92[a]	0.0486	0.4328	0.5186
10	0.0221	0.2906	0.5333	0.1539	2.56		0.0562	0.4922	0.4516
0	0.0216	0.2896	0.4560	0.2329	2.47		0.0588	0.5266	0.4146
32-68-3									
60	0.4002	0.4802	0.1196		1.13	1.14	0.5264	0.4211	0.0524
50	0.434	0.4528	0.1132		1.14		0.5610	0.3902	0.0488
40	0.4686	0.4212	0.1103		1.16		0.5961	0.3572	0.0468
30	0.5522	0.3856	0.0623		1.20		0.6653	0.3097	0.0250
20	0.6205	0.3318	0.0477		1.23	1.16[a]	0.7235	0.2579	0.0185
10	0.7098	0.2902			1.28		0.7858	0.2142	
0	0.6247	0.3753			1.25		0.7140	0.2860	

* Predicted from ^{27}Al NMR.

[a] Measured at 25°C.

Table ESI 3. Conditional equilibrium constants (I = 1.5) for sample 32-66-1 as function of temperature.

T (^{o}C)	pH	K_1	K_2
60	1.89[a]	0.704	0.092
50	1.95[a]	0.549	0.073
40	1.95[a]	0.510	0.078
30	1.96[a]	0.469	0.081
25	1.95[a]	0.408	0.079
20	2.06[a]	0.322	0.052
10	2.14[a]	0.248	0.040
0	2.22[a]	0.227	0.023
25	1.88[b]		
65	1.78[b]		
25	2.0[c]	0.289	0.024

a: estimated from the relative intensities of peaks in the ^{27}Al-NMR spectra and conditional equilibrium constants;

b: direct potentiometric measurement

c: calculated using thermodynamic data.