The Complexation of Al^{III}, Pb^{II} and Cu^{II} Metal Ions by Esculetin: A Spectroscopic and Theoretical Approach

Annaïg Le Person, Aurélien Moncomble, Jean-Paul Cornard

LASIR, CNRS UMR8516, Université Lille 1 Sciences et Technologies, Bât C5 – 59 655 Villeneuve d'Ascq Cedex – France

Supporting Information

Full reference [39] S2

Absorption wavelengths for the aluminum complex depending on the solvatation model S3

Absorption wavelengths for the 2:1 aluminum complex S6

Cartesian coordinates for esculetin and the three 1:1 complexes S7

Full reference [39]

Gaussian 09, Revision D.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, **2009**.

Absorption wavelengths for the aluminum complex depending on the solvatation model

To check the validity of the solvatation model used, in which the first coordination sphere of aluminum(III) is described by explicit molecules (one hydroxide anion and three water molecules) while the bulk is described by an implicit model, we tried to modify the description of the cation environment. From the structure obtained by this first model (denoted M1), we derived some related approaches:

M2 – the structure from M1 without any water molecule or hydroxide anion around Al^{III} but in the presence of an implicit model **without** reoptimization

M3 – the structure from M1 without any water molecule or hydroxide anion around Al^{III} but in the presence of an implicit model **with** reoptimization

M4 – the structure from M1 without any water molecule, but with a hydroxide anion around Al^{III} and in the presence of an implicit model **without** reoptimization

M5 – the structure from M1 without any water molecule, but with a hydroxide anion around Al^{III} and in the presence of an implicit model **with** reoptimization

The wavelengths calculated for each of these models is reported in Table S1.

These results illustrate that models M2, M3 and M4 lead to too weak transitions (see the oscillator strengths) around the observed one, but also some lower energy transitions inconsistent with the measurement. Model M5 did not present these defaults but the lowest energy transition is computed at 335 nm (3.70 eV, f = 0.316), outside of the confidence interval generally accepted for TD-DFT computed transition energies (0.3 eV). As a conclusion, only model M1 is able to reproduce the experimental wavelengths that justifies its use for the whole study. It confirms the fact that water molecules act both as solvent and as ligands of the metal cation. Moreover, it allows us to study the deprotonation of water molecules in order to take into account the influence of pH, that cannot be realized with an implicit solvent.

To check if this conclusion is related to the difficulty created by the hydroxide anion, we proceeded to the same study for copper(II) and lead(II) complexes in which this issue is not present. For these two cases, results are reported in Table S2 for derived models M'1, M'2 and M'3.

Once again, only model M'1 leads to a good reproduction that confirms the tendency observed for aluminum(III): the consideration of explicit molecules is crucial to take into account the solvent.

Table S1: Wavelength and energy of transition calculated between 350 nm and 425 nm for aluminum(III) complexes with each model, discrepancy with the experimental values and oscillator strengths for transitions with an oscillator strength higher than 0.01 (Y is for Yes and N for No).

Model	Explicit water	Explicit hydroxide	Reoptimized	Transitions between 350 nm and 425 nm		
				λ_{abs} (nm, eV)	$\Delta\lambda$ (nm, eV)	f
M1	Y	Y		**380 (3.26)**	**5 (0.04)**	**0.309**
M2*	N	N	N	390 (3.18)	5 (0.04)	0.031
M3*	N	N	Y	356 (3.48)	29 (0.26)	0.051
M4*	N	Y	N	421 (2.94) 373 (3.33)	36 (0.28) 12 (0.11)	0.040 0.068
M5	N	Y	Y	-	-	-
experiment				*385 (3.22)*		

* for these models, lower energy transitions with high oscillator strengths were obtained.

Table S2: Wavelength and energy of transition calculated between 350 nm and 425 nm for each model, discrepancy with the experimental values and oscillator strengths for spin-allowed transitions with an oscillator strength higher than 0.01 (Y is for Yes and N for No).

Cation	Model	Explicit water	Reoptimized	Transitions between 350 nm and 425 nm		
				λ_{abs} (nm, eV)	$\Delta\lambda$ (nm, eV)	f
Cu^{II}	M'1	Y		**385 (3.22)** **353 (3.51)**	**0 (0.00)** **32 (0.29)**	**0.317** **0.027**
	M'2*	N	N	-	-	-
	M'3*	N	Y	402 (3.08)	17 (0.14)	0.251
	experiment			*385 (3.22)*		
Pb^{II}	M'1	Y		**383 (3.24)**	**2 (0.02)**	**0.447**
	M'2*	N	N	359 (3.45)	26 (0.23)	0.180
	M'3	N	Y	420 (2.95) 352 (3.52)	35 (0.27) 33 (0.30)	0.371 0.127
	experiment			*385 (3.22)*		

* for these models, lower-energy transition with high oscillator strengths were obtained.

Absorption wavelengths for the 2:1 aluminum complex

As in the main text of this article, case (i) refers to a fixation of the second aluminum on the lactone moiety while case (ii) refers to the fixation of an aluminum dimer on the catechol moiety. Al1 is the aluminum atom directly bound to the catechol moiety while Al2 is the other one. The coordination sphere of aluminum ion is always considered to contain six ligands.

Case (i):

Table S3: Nature of the coordination sphere, wavelength and energy of the lowest-energy transition for some hypothetical structures and oscillator strengths.

Al1		Al2		Lowest-energy transition	
water	hydroxide	water	hydroxide	λ_{abs} (nm, eV)	f
4	0	5	0	397 (3.12)	0.291
3	1 ax.	5	0	423 (2.93)	0.267
3	1 eq.	5	0	419 (2.96)	0.265
3	1 ax.	4	1 eq.	409 (3.03)	0.291
3	1 ax.	3	2 eq.	401 (3.09)	0.304
3	1 ax.	2	1 ax. and 2 eq.	396 (3.13)	0.306

Case (ii):

Table S4: Nature of the coordination sphere, wavelength and energy of the lowest-energy transition for some hypothetical structures and oscillator strengths.

Al1			Al2		Lowest-energy transition	
water	μ^1 hydroxide	μ^2 hydroxide	water	μ^1 hydroxide	λ_{abs} (nm, eV)	f
1	0	3	3	0	377 (3.29)	0.325
1	0	3	2	1	383 (3.24)	0.325
0	1	3	3	0	397 (3.12)	0.320
2	0	2	4	0	366 (3.39)	0.328
2	0	2	3	1 ax.	376 (3.30)	0.320
2	0	2	3	1 eq.	371 (3.34)	0.331
1	1	2	3	1	387 (3.20)	0.306

Cartesian coordinates for esculetin and the three 1:1 complexes

Optimized geometry of esculetin: cartesian coordinates

C	1.953584	-0.783923	0.000009
C	0.684952	-1.344657	-0.000022
C	-0.418518	-0.496091	-0.000029
C	-0.276438	0.899145	-0.000012
C	1.022993	1.444831	0.000022
C	2.127850	0.619760	0.000028
H	0.546002	-2.418939	-0.000055
C	-1.475596	1.684859	-0.000026
H	1.160473	2.519471	0.000050
C	-2.695430	1.094382	-0.000048
C	-2.833426	-0.345630	-0.000066
H	-1.393041	2.766318	-0.000015
H	-3.613852	1.664961	-0.000050
O	-1.659070	-1.080140	-0.000061
O	-3.875322	-0.973306	-0.000039
O	3.383177	1.155156	0.000036
H	4.031336	0.437134	0.000269
O	3.109816	-1.502076	0.000007
H	2.940430	-2.452176	0.000243

Optimized geometry of aluminum(III) complex (structure D): cartesian coordinates

C	-0.137068	-0.577072	0.113812
C	1.097368	-1.223996	0.129669
C	2.255067	-0.453507	0.046384
C	2.216983	0.948561	-0.053108
C	0.953769	1.596946	-0.071003
C	-0.209347	0.859799	0.009810
H	1.157263	-2.302787	0.206058
C	3.465332	1.629671	-0.130404
H	0.908544	2.677808	-0.148778
C	4.649273	0.954096	-0.110692
C	4.682850	-0.480034	-0.011049
H	3.464902	2.712535	-0.206806
H	5.603037	1.460345	-0.169043
O	3.458142	-1.121393	0.064876
O	5.676937	-1.192127	0.013648
O	-1.450984	1.364831	-0.004085
O	-1.305936	-1.197880	0.188688
Al	-2.722250	0.026491	0.184301
H	-4.365106	1.802023	-0.849932
H	-4.559504	1.664693	0.711187
H	-2.695526	-0.293731	2.560766
H	-4.568515	-1.668719	0.526613
H	-3.415091	-2.391403	-0.215652
H	-3.165888	-0.659610	-2.429420
H	-2.069024	0.452784	-2.369788
O	-3.277937	0.075438	1.894359
O	-4.293507	1.203915	-0.096020
O	-3.926126	-1.569079	-0.190513
O	-2.823357	0.073296	-1.902080

Optimized geometry of copper(II) complex (structure D): cartesian coordinates

C	-0.218443	-0.621622	0.016490
C	1.027090	-1.253322	-0.000169
C	2.176511	-0.469222	-0.004512
C	2.122848	0.936260	0.009371
C	0.852394	1.566945	0.027450
C	-0.305233	0.813035	0.031922
H	1.096680	-2.334286	-0.012098
C	3.363448	1.635721	0.002809
H	0.792838	2.649963	0.037902
C	4.554846	0.973537	-0.017285
C	4.604557	-0.463812	-0.032789
H	3.350894	2.721139	0.013749
H	5.503239	1.493024	-0.023063
O	3.387575	-1.123501	-0.024321
O	5.607313	-1.163766	-0.052545
O	-1.542804	1.336114	0.049636
O	-1.365857	-1.290884	0.016897
H	-5.130526	1.245002	0.392648
H	-3.950568	2.201594	0.062771
H	-4.869454	-1.694647	0.557983
H	-3.611040	-2.454321	0.058751
O	-4.305666	1.317588	-0.105065
O	-4.111753	-1.632334	-0.038506
Cu	-2.825559	-0.061306	0.031773

Optimized geometry of lead(II) complex (structure D): cartesian coordinates

O	-6.512689	-1.028453	-0.037157
C	-5.478273	-0.376891	-0.020148
O	-4.295154	-1.088304	-0.123326
C	-3.055055	-0.490232	-0.117741
C	-2.935548	0.906495	-0.003150
C	-4.140171	1.659034	0.103980
C	-5.360577	1.052440	0.096192
H	-6.283118	1.610824	0.176497
H	-4.075640	2.738951	0.193153
C	-1.637473	1.473458	-0.004282
C	-0.513874	0.676862	-0.115309
C	-0.663977	-0.754325	-0.232938
C	-1.945205	-1.318200	-0.231126
H	-2.067116	-2.390809	-0.319876
H	-1.524167	2.548585	0.082958
O	0.432104	-1.484773	-0.342343
O	0.736717	1.163846	-0.123446
Pb	2.315413	-0.320962	-0.322252
O	2.106860	-1.017187	2.075876
H	2.870545	-1.169957	2.647449
H	1.513600	-1.771065	2.195036
O	3.011149	1.987945	0.987645
H	2.060099	2.190145	0.946700
H	3.262282	2.042615	1.917095