

## Decisive role of $Al^{3+}$ cation in the electrodetosylation of N, N'-bis-(*o*-tosylaminophenyl) Propanediamide to N, N'-bis-(*o*-aminophenyl) Propanediamide

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**Resume :** The reductive electrodetosylation of N, N'-bis-(*o*-tosylaminophenyl) propanediamide was performed in an undivided cell fitted with a sacrificial aluminum anode, at constant current and at room temperature. The completion of the reduction process was favoured by the complexing effect of the anodically generated metal ion to form Al - N, N'-bis (*o*-aminophenyl) propanediamide. Finally, the N, N'-bis (*o*-aminophenyl) propanediamide is obtained by hydrolysis of the Al - complex. © 1997 Elsevier Science Ltd.

As part of the synthesis of new metal complexes of dibenzo[*b,i*]-1,4,8,11-tetraaza[14]annulenes dissymmetrically substituted in the pentane diiminato rings<sup>1</sup>, we want to synthesize a new key-molecule : N, N'-bis-(*o*-aminophenyl) propanediamide by electrochemical detosylation of N, N'-bis-(*o*-tosylaminophenyl) propanediamide in which propanediamide is a vulnerable function.

A tosyl group is a valuable protective group of a primary or secondary amine as well as a synthetic tool in wide use in organic chemistry, but one of the drawbacks resides in the difficulty of its removal. Sulfonamides are generally not hydrolyzed by alkaline treatment, not even with hot concentrated alkali. However hot acid hydrolyzes them. Sometimes, the hydrolysis conditions are hard for a N-functional tosylamide<sup>2</sup>.

Nevertheless the tosyl protecting group of amines can be removed by the cathodic cleavage (electroreduction) of the N-S bond. Mild reaction conditions and the possibility of smooth variation in the strength of reagent (electron at electrode) by merely changing its potential makes electrolysis a very attractive method for such conversion<sup>3</sup>.

With a sacrificial aluminum anode, we realized for the first time, to our knowledge, a total deprotection of a ditosylated compound. A propanediamidoaluminum complex was isolated at the end of the electrolysis. The present paper reports such electrolysis and the decisive role of electrogenerated aluminum cation during the electrolysis.

### RESULTS

Generally an amide group can be prepared by conversion of an ester group with the corresponding amine. However no amide formation was observed by heating the phenylenediamine and diethyl malonate.

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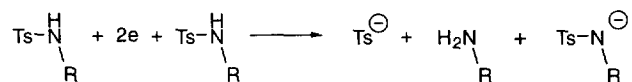
Conversely, the few soluble N, N'-bis-(*o*-tosylaminophenyl) propanediamide in ethanol at room temperature became soluble with decomposition in hot ethanol. N-(*o*-aminophenyl) tosylamide and diethyl malonate were isolated as the main products. So, propanediamide is a vulnerable function.

The direct condensation of malonyl chloride and phenylenediamine yielded 2,3-benzo-1H, 1,4-diazacycloheptene-5,7-dione. So, the amine protection was necessary.

Heating N, N'-bis-(*o*-tosylaminophenyl) propanediamide with aluminum or sodium-amalgam in THF containing 15 to 20% methanol did not give any reduced product but a deprotonated product. The structure was not determined. Washing this one with water or HCl gave N, N'-bis-(*o*-tosylaminophenyl) propanediamide.

### Electrochemistry of N, N'-bis-(*o*-tosylaminophenyl) propanediamide

In the literature, tosylamide S-N bond cleavage was explained by a direct electrochemical reduction. EEC mechanism was proposed in aprotic solvent and ECEC mechanism for protic medium. The S-N bond is broken after the second electron transfer. The significant influence of the experimental conditions made that the mechanism could not be given with absolute certainty<sup>4</sup>. For example, the electroreduction of primary tosylamide which possesses a mobile proton has a ECEC mechanism in aprotic solvent as acetonitrile.



The electric balance apparently is one electron per molecule because a half of starting substance is not reduced but is used as the proton source. The chemical yield can not be more than 50%<sup>5,6</sup>.

In this context, it was interesting to know the electrochemical behaviour of N, N'-bis-(*o*-tosylaminophenyl) propanediamide and to compare it with monotosylamide.

The reduction of N, N'-bis-(*o*-tosylaminophenyl) propanediamide was quickly examined, by cyclic voltammetry, in acetonitrile with 0,1M NBu<sub>4</sub>I, at a vitreous carbon disc electrode (Fig 1a). The potential scan rate was in the range from 10 to 100 mV/s.

The cyclic voltammogram of the N, N'-bis-(*o*-tosylaminophenyl) propanediamide has a large peak of reduction at -2.20 V/SCE. The peak potential is very near the solvent reduction potential. This peak is not chemically reversible indicating that the reduction is not a pure electrochemical process at the electrode surface but a combined electrochemical and chemical process.

Addition of phenol in the solution increases the peak current (curve 3 of Fig 1a).

Further interpretation of these data is postponed until a more consistent kinetic work is completed.

However, the ditosylated propanediamide seems to follow an electrochemical behaviour close to that a mono-tosylated, if so, the N, N'-bis-(*o*-tosylaminophenyl) propanediamide with two tosyl groups is expected to be totally detosylated through a four-electron reduction, in the absence of autoprotonation processes.

In methyl alcohol + 0.1 M NMe<sub>4</sub>Br and on a vitreous carbon disc electrode, the cyclic voltammogram shows two irreversible reduction peaks, at -1.07 and -1.40 V/SCE (curve 1 of Fig 1b).

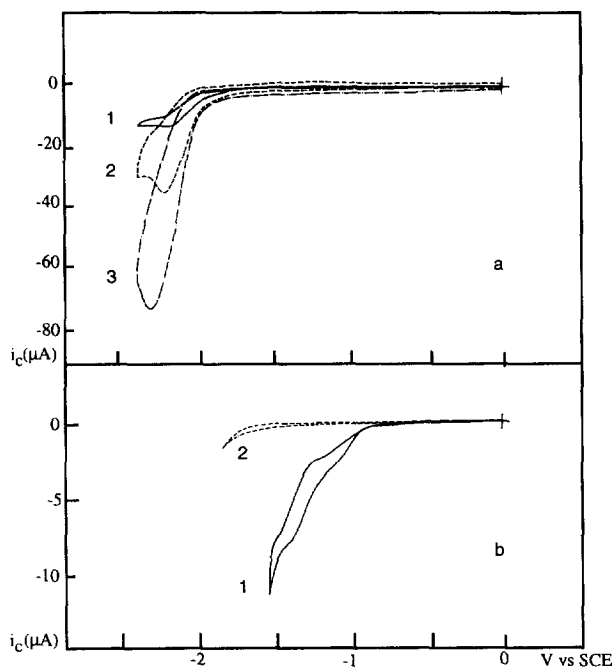


Fig. 1

a) Cyclic voltammogram obtained in a solution containing  $1.01 \times 10^{-3}$  M N, N'-bis-(*o*-tosylaminophenyl) propanediamide +  $\text{CH}_3\text{CN}$  + 0.1 M  $\text{NBu}_4\text{PF}_6$

Curve 1 :  $v = 10$  mV/s

Curve 2 :  $v = 100$  mV/s

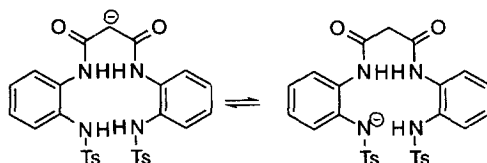
Curve 3 : with  $3.5 \times 10^{-3}$  M PhOH,  $v = 100$  mV/s

b) Curve 1 : Cyclic voltammogram obtained in a solution containing  $8.34 \times 10^{-4}$  M N, N'-bis-(*o*-tosylaminophenyl) propanediamide +  $\text{CH}_3\text{OH}$  + 0.1 M  $\text{NMe}_4\text{Br}$ ,  $v = 10$  mV/s

Curve 2 : with  $8.65 \times 10^{-4}$  M KOH added

Working electrode : Vitreous carbon disk of  $s = 7.85 \times 10^{-2}$  cm<sup>2</sup> surface area.

The reduction peaks completely disappeared when one equivalent of base, for example, KOH was added (curve 2b). It is very likely that the deprotonated form of N, N'-bis-(*o*-tosylaminophenyl) propanediamide is not reducible. The proton between the  $\alpha$  and  $\gamma$  carbonyls is mobile. However, the tosylamide may also be deprotonated by the action of a strong base<sup>7</sup>. We could not specify completely the main deprotonated form. In our case, these two forms were in equilibrium and they are not electrochemically reducible.



This observation could explain the failure of Na and Al-amalgam reduction in alcoholic THF : as the tosylamide reduction potential is very near the solvent reduction potential, this treatment was not chemically selective. The solvent reduction gives an alcoholate which is a strong base, capable to deprotonate N, N'-bis-(*o*-tosylaminophenyl) propanediamide. The deprotonated form of N, N'-bis-(*o*-tosylaminophenyl) propanediamide is not reducible. Therefore no reduction has been observed.

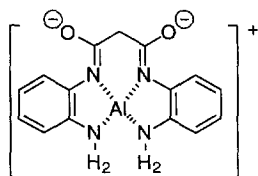
### Electrolysis aspect

The sacrificial anode method is a relatively recent technique in electrosynthesis<sup>8,9</sup>. The anodic

compartment of a double compartment cell is replaced by an easily oxidizable metal. A magnesium, aluminum or zinc anode is used and a tetraalkylammonium salt is added as supporting electrolyte at very low concentration. During the electrolysis, the conductivity of the medium is ensured by the electrogenerated ions. The metallic cation from the anode oxidation can stabilize the carbanion and also favour several reactions<sup>8,10</sup>, for example, the cyclization<sup>11,12</sup>. Controlled current electrolysis with a sacrificial anode is the simplest method of electrolysis.

The controlled current electrolysis technique using a sacrificial aluminum anode in different solvents (acetonitrile + 0.1 M NBu<sub>4</sub>I and methanol + 0.1 M NMe<sub>4</sub>Br) was performed with a vitreous carbon cell which served as the cathode. The electrode area was about 40 cm<sup>2</sup>.

As the solubility of the N, N'-bis-(*o*-tosylaminophenyl) propanediamide is very low, about 2x10<sup>-3</sup> M, it strongly influences the electrolysis current. A very low current density (0.25 to 1 mA/cm<sup>2</sup>) is used. The end of the reaction was indicated by a sudden increase of the potential in acetonitrile or by a visible release of hydrogen in methanol<sup>13</sup>. A complex of aluminum was isolated as the main product after electrolysis :



Its formation will be discussed in the following part. Some results of electrolysis are summarized in table 1.

For comparison, the results with a double compartment cell in controlled potential and controlled current electrolysis on a 3 cm<sup>2</sup> vitreous carbon electrode in acetonitrile with 1 M NBu<sub>4</sub>I were cited in the same table.

Table 1 Reduction of N, N'-bis-(*o*-tosylaminophenyl)propanediamide

| Cell                            | Solvent + electrolyte             | Potential or current | n electrons/molecule |
|---------------------------------|-----------------------------------|----------------------|----------------------|
| 1 compartment + Al <sup>a</sup> | acetonitrile + NBu <sub>4</sub> I | 40 mA                | 3.99                 |
|                                 | methanol + NMe <sub>4</sub> Br    | 10 mA                | 4.01                 |
|                                 | "                                 | 30 mA                | 4.10                 |
|                                 | "                                 | 50 mA                | 4.32                 |
| 2 compartments <sup>b</sup>     | acetonitrile + NBu <sub>4</sub> I | -2.50 V/SCE          | 0.94                 |
|                                 | "                                 | 1 mA                 | 1.01                 |

a) 2mmol N,N'-bis-(*o*-tosylaminophenyl)propanediamide dispersed in the solvent + 0.1M electrolyte. A vitreous carbon cell as cathode, aluminum as anode.

b) 0.5mmol N,N'-bis-(*o*-tosylaminophenyl)propanediamide in acetonitrile + 1M NBu<sub>4</sub>I. A 3 cm<sup>2</sup> vitreous carbon plate as cathode and a 3cm<sup>2</sup> platinum plate as anode.

First, in the presence of a sacrificial aluminum anode, the reaction consumes 4 electrons per molecule in acetonitrile. This number corresponds to a four-electron reduction of the two tosylamide groups present in the molecule. On the contrary, this number could not go beyond one electron per molecule whatever the electrolytical method used with a double compartment cell.

Second, acetonitrile is an aprotic solvent and methanol is protic. The electron number per molecule is four in acetonitrile as well as in methanol. The total reduction has not been influenced by the solvent nature. Besides electron, the reduction would need more than 2 protons per molecule, where was the source of the proton in acetonitrile ?

Third, the electron number per molecule increases with the current in methanol. This is normal, due to the reduction of the solvent. The reduction lost its chemical selectivity if the current was important.

At last, the methanol reduction gives methanolate which is a strong base, as in the case of amalgam reduction, the reduction would be stopped. However, the total reduction has not been perturbed by the base presence.

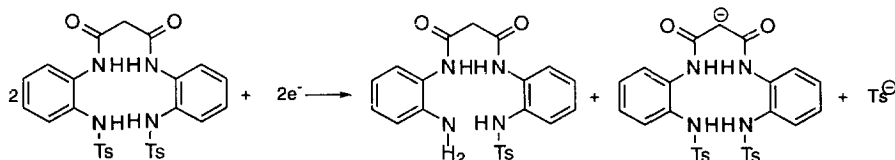
Consequently, electrogenerated Al<sup>3+</sup> ion has a promoting action on the total detosylation.

### Role of Al<sup>3+</sup> cation

The constant potential and controlled current electrolyses of N, N'-bis-(*o*-tosylaminophenyl) propanediamide in acetonitrile in a diaphragm cell were a one electron reduction. This result seems to indicate the following points :

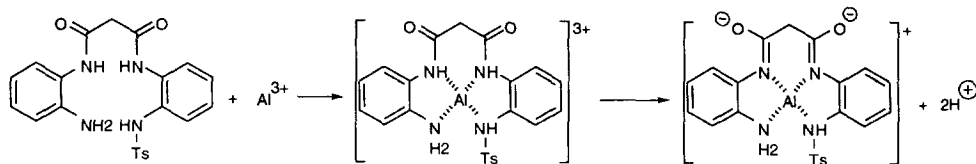
- 1) The two tosylamide groups are not reduced simultaneously at the cathode.
- 2) Only one half of N, N'-bis-(*o*-tosylaminophenyl) propanediamide is reduced with 2 electrons and another half of starting material is used as the proton source.
- 3) The absence of the second tosyl reduction would indicate that the N-(*o*-aminophenyl), N'-(*o*-tosylaminophenyl) propanediamide may not be reducible under the present electrolysis conditions.
- 4) The deprotonated form of N, N'-bis-(*o*-tosylaminophenyl) propanediamide is not reducible.

The over all reaction in acetonitrile could be written as follows :



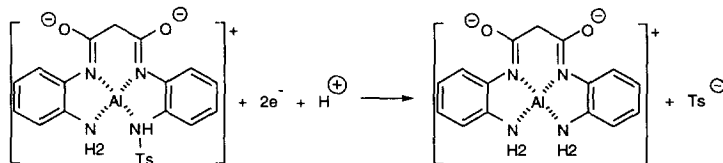
N, N'-bis-(*o*-aminophenyl) propanediamide is a new propanediamide ligand. Analogous propanediamido-metal complex was already reported in the literature<sup>14-19</sup>. The complexation power is depending the number of amine groups present in the molecule<sup>20</sup>. Consequently, the precursor, N, N'-bis-(*o*-tosylaminophenyl) propanediamide, without amine function, could not be a good ligand for Al<sup>3+</sup>. In N, N'-bis-(*o*-aminophenyl) propanediamido-aluminum complex we observe a good metal-ligand affinity. N-(*o*-aminophenyl), N'-(*o*-tosylaminophenyl) propanediamide will be an intermediate possessing a complexing power between the precursor and final ligand.

In the presence of electrogenerated Al<sup>3+</sup> cation, by analogy, an intermediate complex is formed after the first tosyl reduction :

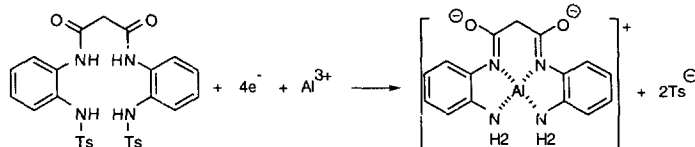


This complexation is accompanied by the release of two protons in the medium. This formation is, of course, the source of proton in acetonitrile.  $\text{Al}^{3+}$  cation is a strong Lewis acid so the reaction is not influenced by the acidity of solvent (acetonitrile or methanol).

The new complex intermediate has a positive charge, the continuous reduction at cathode may be favoured,



The complete reduction of N, N'-di-(*o*-tosylaminophenyl) propanediamide is four electron.



It was demonstrated that the stabilisation of carbanion by the electrogenerated metal ion is usually an interaction between 2 charged entities, carbanion and metallic cation. This stabilization aims at increasing the lifetime of carbanion<sup>10,11</sup>.

In our case, the electrogenerated aluminum cation is inactive in the first tosyl reduction swing to the no complexation power of N, N'-bis-(*o*-tosylaminophenyl) propanediamide. This reduction is identical in a single or double compartment cell.

After the first tosyl reduction, the electrogenerated aluminum cation reacts with N-(*o*-aminophenyl), N'-(*o*-tosylaminophenyl) propanediamide. This amino-propanediamido ligand is electrically neutral. The interaction is accompanying the coordination bond formation and the release of proton. The aluminum cation is not expelled after the second tosyl reduction. Therefore, it can be assumed that aluminium cation does not play completely the role of a chemical catalyst not either of carbanion stabilizer. It plays the role in molecular activation by complexation. This complexation makes a non reducible intermediate to an intermediate-aluminum complex which is again reducible at the cathode.

## CONCLUSION

The N, N'-bis-(*o*-aminophenyl) propanediamide can be prepared by electrochemical deprotection of the N, N'-bis-(*o*-tosylaminophenyl) propanediamide. This synthesis was achieved by taking advantage of the Al<sup>3+</sup> activation of the molecule.

The activation of tosylamide by electrogenerated Al<sup>3+</sup> cation was examined for the first time in electrodetosylation. This observation offers a smooth condition to some molecule possessing a complexation power as peptides, paracyclophanes and polyazamacrocycles in which the tosyl is often used as the removable protective group of amine function.

The experimental conditions will be optimised.

## EXPERIMENTAL SECTION

### Reagents

The phenylenediamine, *p*-toluenesulfonyl chloride, sodium hydride 60% in mineral oil were purchased from ACROS ; the malonyl chloride from Fluka ; the solvent THF, from SDS, was distilled over sodium and benzophenone under argon.

All chemicals were used as received : electrochemical grade tetrabutylammonium iodide and tetramethylammonium bromide (Fluka), Gen-apex grade anhydrous acetonitrile (water < 0.005%) (Prolabo), RPE grade methyl alcohol and ethyl alcohol (Carlo-Erba). A rod of aluminum ( $\phi$  8 mm, Normapur) was obtained from Prolabo and used as anode in the electrolysis.

### Apparatus

All <sup>1</sup>HNMR spectra were recorded on a Bruker AC-250 or 200 using TMS as the internal standard. Elemental analyses were obtained from the Service de Microanalyse, CNRS de Gif sur Yvette, France.

IR spectra were recorded on a Bruker IFS 66 Fourier transform apparatus. The samples were prepared with IR grade potassium bromide (Fluka).

Melting points were determined on a Kofler bench or on a BUCHI 510.

All cyclic voltammograms were obtained on a set composed of a home-made potentiostat, a EG&G 175 signal generator and a Kipp & Zonen BD90 X,Y recorder. The constant potential was performed with a Tacussel PRT 100-1X potentiostat and the constant intensity electrolysis with a home-made current generator (15V-1A). The current was integrated with a home-made integrator (100  $\mu$ A - 500 mA).

The reference electrode was a saturated calomel electrode (SCE) (TACUSSEL) and a Pt plate electrode as counter-electrode. The working electrode is a disc of 0.07 cm<sup>2</sup> vitreous carbon (Le Carbone Lorraine) in cyclic voltammetry using a unthermostated cell at room temperature; a plate of 3 cm<sup>2</sup> vitreous carbon (Le Carbone Lorraine) in controlled electrolysis using a two compartment cell and a vitreous carbon cell ( $\phi$  40 mm x 40 mm) (Le Carbone Lorraine) in controlled intensity electrolysis for large scale electrolysis.

### N-Tosyl phenylenediamine

0.120 mol of sodium hydride was added to 0.100 mol of *o*-phenylenediamine in 200 ml of freshly distilled THF. To this stirred suspension, under an argon atmosphere, a solution of 0.100 mol *p*-

toluensulfonyl chloride in 100 ml THF was added dropwise for 6-8 hours. The mixture was strongly stirred for a night. A white precipitate was formed from the mixture. After addition of 5 ml of water the mixture was cooled in an ice bath. The precipitate was filtered off. The filtrate was evaporated under reduced pressure. The crude product was recrystallized from 50 to 100 ml refluxing diethyl ether. *N*-tosyl *o*-phenylenediamine was collected by filtration, washed two times with 15 ml diethyl ether. Dry at 40°C in vacuum (< 0,05 mmHg).

<sup>1</sup>H NMR (ppm in CDCl<sub>3</sub>) : 2.41(s, 3H), 4.14(s, 1H), 6.50(s, 2H), 6.72(d, 1H), 7.00(m, 1H), 7.23(m, 3H), 7.62 (m, 2H), 8.61(d, 1H)

mp : 138°C

IR : 1623cm<sup>-1</sup>, 1408cm<sup>-1</sup>, 1325cm<sup>-1</sup>, 1150cm<sup>-1</sup>, 1092cm<sup>-1</sup>

*N, N'*-bis-(*o*-tosylaminophenyl) propanediamide

To a suspension of 50 mmol of *N*-tosyl phenylenediamine and 58 mmol of sodium hydride in 150 ml of freshly distilled THF, a solution of 25 mmol of malonyl chloride in 40 ml freshly distilled THF was added dropwise under a argon atmosphere with a strougly stirring for 6-8 hours.

After two days, 10 ml of water were added dropwise to the mixture. The solid was filtered off. The filtrate was evaporated under reduced pressure. Mix the two solids in a stirred 100 ml 1M HCl. The solid was filtered, washed with water and dried under reduced pressure.

The dried solid was washed with CH<sub>2</sub>Cl<sub>2</sub>. The product has a white colour, 11.95 g (19.6 mmol), 78% yield.

<sup>1</sup>H NMR (ppm in acetone d<sub>6</sub>) : 2.32(s, 6H), 3.51(s, 2H) 7.20(m, 10H), 7.60(m. 6H), 8.15(s, 2H), 9.77(s, 2H)

Elemental analysis : calculated for C<sub>29</sub>H<sub>28</sub>N<sub>4</sub>O<sub>6</sub>S<sub>2</sub> : C : 58.77, H : 4.76, N : 9.45, S : 10.82, found : C : 58.79, H : 4.78, N : 9.48, S : 10.46

mp : 258 °C (decomposition)

IR : 1679cm<sup>-1</sup>, 1653cm<sup>-1</sup>, 1362cm<sup>-1</sup>, 1321cm<sup>-1</sup>, 1189cm<sup>-1</sup>, 1090cm<sup>-1</sup>

### Large scale electrolysis

To a very well washed vitreous carbon cell containing 30 ml of 0.1 M NBu<sub>4</sub>I (or NMe<sub>4</sub>Br) in acetonitrile (or methyl alcohol), 1.19 g (2.0 mmol) of *N, N'*-bis-(*o*-tosylaminophenyl) propanediamide was added. The cell was covered with a glass cap which has a central hole for the sacrificial aluminum anode, and two lateral inlet and outlet for argon circulation. The suspension was stirred.

The electrolysis current was from de 10 to 50 mA. The current was integrated with a current integrator. The cell was the cathode.

A white gray precipitate was formed during the electrolyses.

After the electrolysis, the mixture was filtered. The solid was washed one or two times with a small volume of the solvent used, three times with diethyl ether then dried (≈ 0.6g).

The solid was added in 5 ml of 1.5 M HCl solution. The mixture was stirred for 10 min. The precipitate was filtered off (≈ 0.08 g).

The pH value of the filtrate was adjusted to between 4 and 5 with a saturated KHCO<sub>3</sub> solution. The



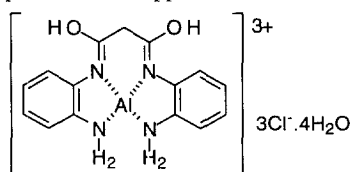
N, N'-bis-(*o*-aminophenyl) propanediamide was precipitated ( $\approx 0.3$  g). The pure product was obtained by filtration on a chromatographic silica-gel column ( $\phi$  2 cm  $\times$  3 cm) using an acetonitrile-dichloromethane (50 : 50) mixture as eluent.  $R = 0.3$  with the acetonitrile-dichloromethane (2 : 1/v : v) mixture. 0.17g, 30% yield. <sup>1</sup>H NMR data in DMSO  $d_6$  : 3.49(s, 2H), 4.98 (s, 4H), 6.52 (t, 2H), 6.70 (d, 2H), 7.93 (t, 2H), 7.11 (d, 2H), 9.37 (s, 2H).

Elemental analysis : calculated for C<sub>15</sub>H<sub>16</sub>N<sub>4</sub>O<sub>2</sub> : C : 63.36, H : 5.67, N : 19.71, found : C : 63.08, H : 5.73, N : 19.61

mp : 247°C (decomposition)

IR : 1657cm<sup>-1</sup>

If the pH > 6, the complex of N,N'-bis-(*o*-aminophenyl) 1,3-dihydroxy-1,3-propadiiminoaluminum chloride tetrahydrate was the major product. The supposed structure is



<sup>1</sup>H NMR data in DMSO  $d_6$  : 3.65 (s, 2H), 7.20(m, 2H), 7.24 (m, 4H), 7.39(m, 2H), 10.69 (s, 2H).

Elemental analysis : calculated for C<sub>15</sub>H<sub>24</sub>AlCl<sub>3</sub>N<sub>4</sub>O<sub>6</sub> : C : 36.94, H : 4.55, N : 11.49, Cl : 21.81. Found : C : 36.32, H : 4.64, N : 11.29, Cl : 21.32

mp : 254°C (decomposition)

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