

Complexes of adrenaline with some divalent transition-metal ions

S. Materazzi*, C. Nugnes, A. Gentili, R. Curini

Department of Chemistry, University of Roma La Sapienza, p. le A. Moro 5, 00185 Rome, Italy

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Abstract

A thermoanalytical study of different adrenaline coordination compounds with some divalent transition-metal ions such as Co(II), Ni(II) and Cu(II) is reported. The solid precipitated compounds were characterized by elemental analysis and by thermogravimetric analysis also coupled to FTIR spectroscopy to analyze the evolved gases and make consistent the proposed decomposition steps.

Several complexes were obtained with the metal/ligand molar ratios of 1:2, 1:4 and 1:6. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

The coordination compounds that epinephrine, commonly also called adrenaline (adr), form with divalent transition metal-ions, such as Co(II), Ni(II) and Cu(II), can be useful models to complete the informations regarding the complexing behaviour of catecholamines and to find out correlations of the properties of these compounds in solution with the properties of them in the solid state.

Different studies of this kind of complexes can be found in the literature [1–8], but few thermoanalytical data are reported for them and there is no information about the decomposition steps that can be directly related with the coordination energies of each complex.

The aim of this work is to compare the thermoanalytical properties of the solid complexes obtained

after precipitation from aqueous or ethanolic solutions using several metallic(II) nitrate/adrenaline (M/L) molar ratios.

The obtained compounds showed M/L molar ratios of 1:2, 1:4 and 1:6, with successive ligand molecules being coordinated to a 1:2 base-unit $[M(L)_2^{2+}]$. The solvent makes the difference, especially in the complexes with more than four coordinated ligand molecules.

The characterization of the solids complexes was performed by elemental analysis, thermogravimetric analysis and coupled TG-FTIR evolved gas analysis.

2. Experimental

2.1. Materials

Adrenaline and the metallic(II) salts were from Aldrich and were used without further purification. All the solvents used were of RPE grade.

* Corresponding author. Tel.: +39-6-49913616;
fax: +39-6-4453616.

E-mail address: smaterazzi@uniroma1.it (S. Materazzi).

2.2. Syntheses of the complexes

All the complexes were precipitated from aqueous solutions at pH = 4 and from ethanolic solutions, with the same starting Me/adr ratios.

2.2.1. $[Co(adr)_6](NO_3)_2$

To a solution of Adrenaline (6 mmol) in 250 ml of absolute ethanol, a solution of $Co(NO_3)_2 \cdot 3H_2O$ (1 mmol) in 250 ml of absolute ethanol was added, with heating (50°C) and stirring. The solid formed was washed with absolute ethanol and dried in vacuo.

2.2.2. $[Co(adr)_4](NO_3)_2$

To a solution of Adrenaline (3.5 mmol) in 250 ml of absolute ethanol, a solution of $Co(NO_3)_2 \cdot 3H_2O$ (1 mmol) was added in 250 ml of absolute ethanol, with heating (50°C) and stirring. The solid formed was washed with absolute ethanol and dried in vacuo.

2.2.3. $[Co(adr)_2](NO_3)_2$

To a solution of Adrenaline (2 mmol) in 250 ml of absolute ethanol, a solution of $Co(NO_3)_2 \cdot 3H_2O$ (1 mmol) in 250 ml of absolute ethanol was added, with heating (50°C) and stirring. The solid formed was washed with absolute ethanol and dried in vacuo.

2.2.4. $[Ni(adr)_6](NO_3)_2$

To a solution of Adrenaline (6 mmol) in 250 ml of absolute ethanol, a solution of $Ni(NO_3)_2 \cdot 5H_2O$ (1 mmol) in 250 ml of absolute ethanol was added, with heating (50°C) and stirring. The solid formed was washed with absolute ethanol and dried in vacuo.

2.2.5. $[Ni(adr)_4](NO_3)_2$

To a solution of Adrenaline (3 mmol) in 250 ml of absolute ethanol, a solution of $Ni(NO_3)_2 \cdot 5H_2O$ (1 mmol) in 250 ml of absolute ethanol was added, with heating (50°C) and stirring. The solid formed was washed with absolute ethanol and dried in vacuo.

2.2.6. $[Ni(adr)_2](NO_3)_2$

To a solution of Adrenaline (1.5 mmol) in 250 ml of absolute ethanol, a solution of $Ni(NO_3)_2 \cdot 5H_2O$ (1 mmol) in 250 ml of absolute ethanol was added, with heating (50°C) and stirring. The solid formed was washed with absolute ethanol and dried in vacuo.

2.2.7. $[Cu(adr)_6](NO_3)_2$

To a solution of Adrenaline (6 mmol) in 250 ml of absolute ethanol, a solution of $Cu(NO_3)_2 \cdot 5H_2O$ (1 mmol) in 250 ml of absolute ethanol was added, with heating (50°C) and stirring. The solid formed was washed with absolute ethanol and dried in vacuo.

2.2.8. $[Cu(adr)_4](NO_3)_2$

To a solution of Adrenaline (3.5 mmol) in 250 ml of absolute ethanol, a solution of $Cu(NO_3)_2 \cdot 5H_2O$ (1 mmol) in 250 ml of absolute ethanol was added, with heating (50°C) and stirring. The solid formed was washed with absolute ethanol and dried in vacuo.

2.2.9. $[Cu(adr)_2](NO_3)_2$

To a solution of Adrenaline (2 mmol) in 250 ml of absolute ethanol, a solution of $Cu(NO_3)_2 \cdot 5H_2O$ (1 mmol) in 250 ml of absolute ethanol was added, with heating (50°C) and stirring. The solid formed was washed with absolute ethanol and dried in vacuo.

2.3. Instrumental

The thermoanalytical curves were obtained using a Perkin-Elmer TGA7 thermobalance (range 20–1000°C); the atmosphere was either pure nitrogen or air, at a flow rate of 100 ml min⁻¹; the heating rate was varied between 5 and 40°C min⁻¹, with the best resolution achieved at a rate of 10°C min⁻¹.

To obtain the IR spectra of the gases evolved during the thermogravimetric analysis, the thermobalance is coupled with a Perkin-Elmer FTIR spectrometer, model 1760X. The TGA7 is linked to the heated gas cell of the FTIR instrument by means of a heated transfer line, and the temperatures of the cell and of the transfer line are independently selected.

3. Results

3.1. Elemental analysis

In Table 1, the resulting values from the elemental analysis are listed.

3.2. Thermal analysis

Figs. 1–3 show the thermogravimetric profiles of the different complexes.

Table 1
Elemental analysis of the precipitated complexes: percentage values found (and calculated)

Complex	C	H	O	N
[Co(adr) ₆](NO ₃) ₂	50.7 (50.54)	6.4 (6.08)	30.0 (29.95)	8.9 (8.73)
[Co(adr) ₄](NO ₃) ₂	47.0 (47.17)	5.8 (5.67)	31.6 (31.45)	9.3 (9.17)
[Co(adr) ₂](NO ₃) ₂	39.0 (39.32)	4.7 (4.73)	34.8 (34.95)	10.2 (10.19)
[Ni(adr) ₆](NO ₃) ₂	50.7 (50.55)	6.1 (6.08)	30.1 (29.95)	8.6 (8.73)
[Ni(adr) ₄](NO ₃) ₂	47.2 (47.18)	5.8 (5.68)	31.6 (31.45)	9.3 (9.17)
[Ni(adr) ₂](NO ₃) ₂	39.3 (39.33)	4.9 (4.73)	35.1 (34.96)	10.3 (10.20)
[Cu(adr) ₆](NO ₃) ₂	50.5 (50.36)	6.1 (6.06)	30.1 (29.84)	8.7 (8.70)
[Cu(adr) ₄](NO ₃) ₂	47.0 (46.94)	5.8 (5.65)	31.1 (31.29)	9.0 (9.12)
[Cu(adr) ₂](NO ₃) ₂	39.0 (38.99)	4.8 (4.69)	34.8 (34.66)	10.3 (10.11)

The cobalt(II), nickel(II) and copper(II) complexes in the M/L ratio of 1:6 show a different thermal stability, the Co(II) complex being slightly more stable than those of Cu(II) and Ni(II) having the lowest thermal stability of them (Fig. 1).

The decomposition steps of the three complexes (air flow) show the release of two adrenaline molecules, followed by the release of another two adrenaline

molecules, and the final decomposition to give the metal oxide. The cobalt complex shows a less marked process for the second step, while the nickel complex shows a splitting of the final decomposition in two well defined TG steps.

Fig. 2 presents the thermogravimetric profiles of the complexes with the M/L ratio of 1:4; they show a very similar thermal stability with air

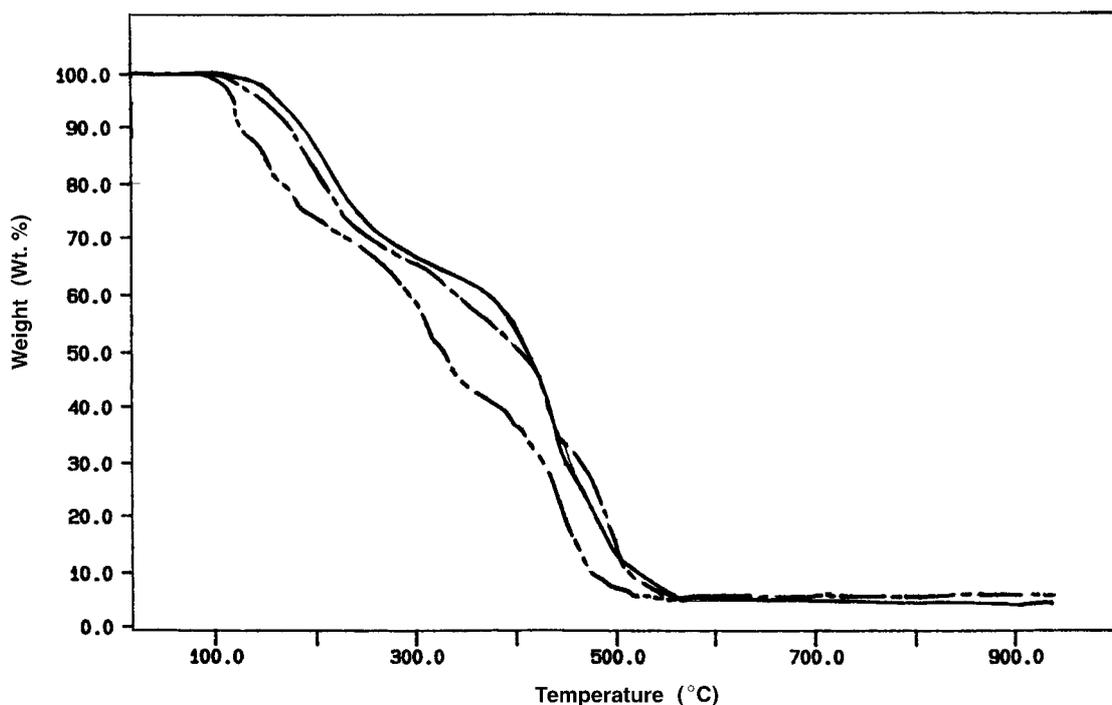


Fig. 1. Thermogravimetric profiles of the [Me(adr)₆](NO₃)₂ complexes. (—) Co(II); (---) Cu(II); (- - -) Ni(II). Scanning rate: 10°C min⁻¹. Air flow rate: 100 ml min⁻¹.

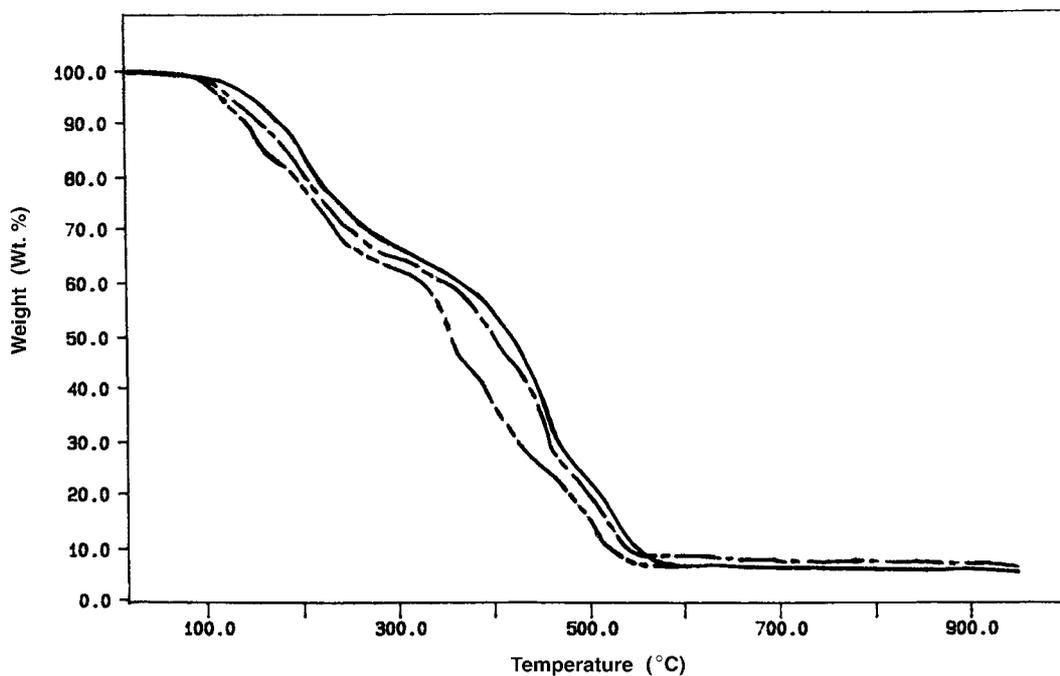


Fig. 2. Thermogravimetric profiles of the [Me(adr)₄](NO₃)₂ complexes. (—) Co(II); (---) Cu(II); (- - -) Ni(II). Scanning rate: 10°C min⁻¹. Air flow rate: 100 ml min⁻¹.

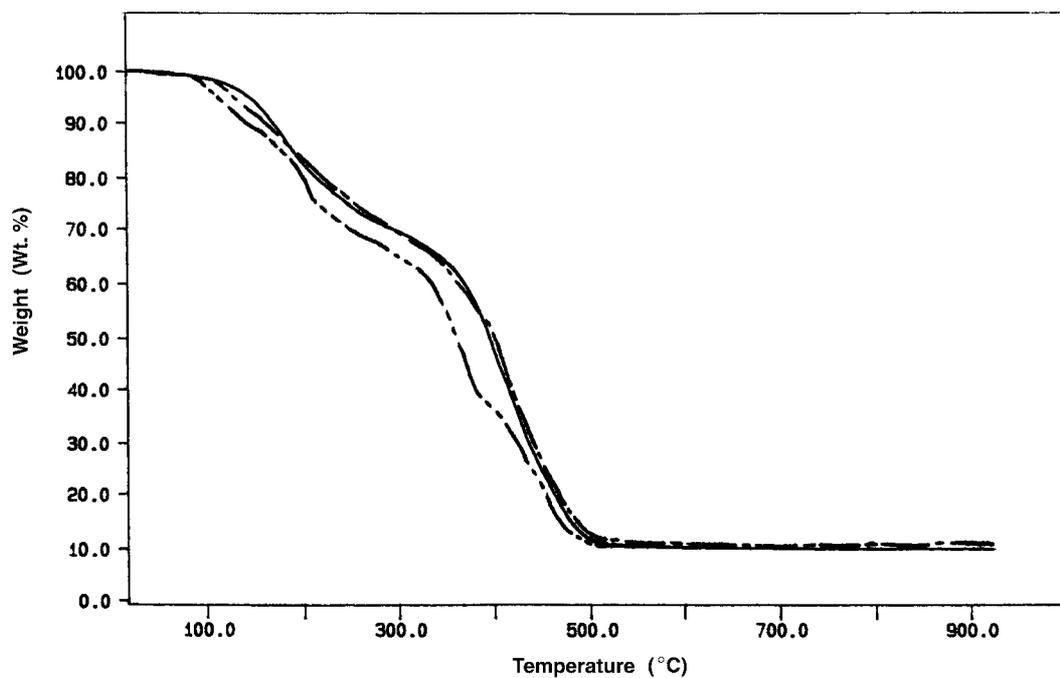


Fig. 3. Thermogravimetric profiles of the [Me(adr)₂](NO₃)₂ complexes. (—) Co(II); (---) Cu(II); (- - -) Ni(II). Scanning rate: 10°C min⁻¹. Air flow rate: 100 ml min⁻¹.

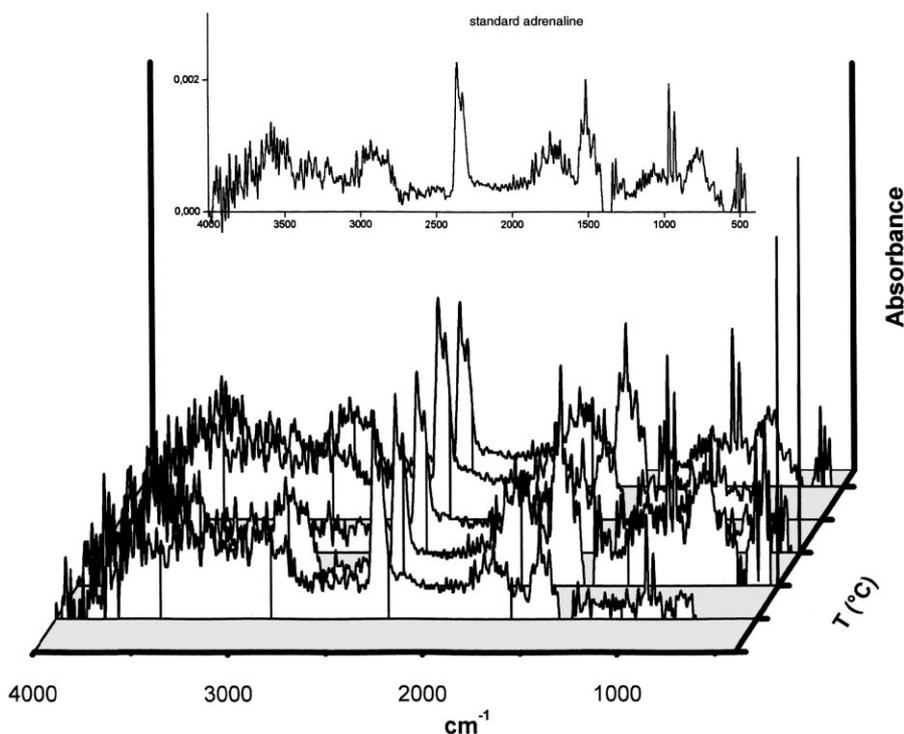


Fig. 4. Infrared spectra of the TG evolved gases for the release of adrenaline molecules. Resolution: 8 cm^{-1} .

flow, with the Co(II) complex more stable than the Cu(II) complex, both more stable than the Ni(II) complex.

The thermal decomposition is characterized by three main decomposition steps, the first being the release of two adrenaline molecules, the second being the loss of the nitrate ions, followed by the final step of oxidation to obtain the metal oxide.

The complexes with a M/L ratio of 1:2 are again characterized by three main steps when heated in air flow; the first with the release of one adrenaline molecule, the second with the loss of the nitrate ions and the third with the final oxidation to give MO. The Cu(II) complex is more stable than the Co(II) complex, with the Ni(II) complex always being the less thermally stable.

The evolved gas analysis, performed by coupling the thermogravimetric analyzer to an infrared spectrometer and with the consequent characterization of the IR bands related to the vapours or gases evolved in the range $20\text{--}350^\circ\text{C}$, supports the proposed decomposi-

tion processes. One representative IR spectrum is shown in Fig. 4.

The thermogravimetric curves of the decomposition under nitrogen flow (not reported) show a similar profile in the temperature range $20\text{--}300^\circ\text{C}$, with the final decomposition step very broad and often not reaching a constant weight at 900°C .

4. Discussion

The thermogravimetric profiles of the solid complexes show an interesting property commonly observed for other coordination compounds prepared in our laboratory: TG curves clearly show the presence of a fundamental 1:2 base-unit for all the 1:4 and 1:6 complexes; this can be deduced from the releasing temperature and because the step height is always equivalent to two ligand molecules before the final decomposition process to obtain the metal oxide.

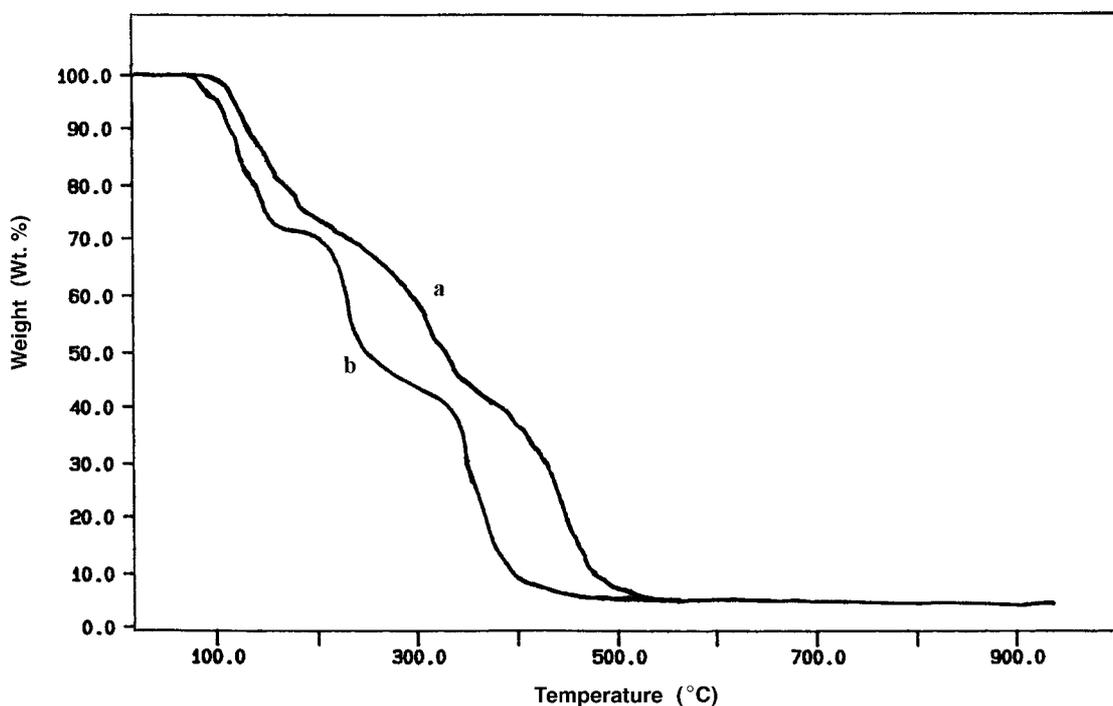


Fig. 5. Thermogravimetric curves of the $[\text{Ni}(\text{adr})_6](\text{NO}_3)_2$ complexes: (a) precipitated from ethanolic solution; (b) precipitated from water solution. Scanning rate: $10^\circ\text{C min}^{-1}$. Air flow rate: 100 ml min^{-1} .

Thus, it can be proposed the coordination to the 1:2 base-unit of two adrenaline molecules, followed by the coordination of another two molecules of adrenaline at a second stage, to form respectively the 1:4 and the 1:6 complex.

The experimental evidence is that the number of coordinated molecules increases with the increasing starting M/L molar ratio.

The analysis of the infrared spectra recorded on the TG effluent gases or vapours, clearly shows that the processes related to the loss of two or four adrenaline molecules are eliminations and not decompositions. The characteristic IR bands of the TG evolved gases are typical of adrenaline and can be attributed to the stretching and bending vibrations of the $-\text{OH}$, $-\text{CH}_3$ and $-\text{NH}_2$ groups.

A possibility of driving the reaction to obtain solids of different thermal stability was observed by using different solvents (water and absolute ethanol). The different solvent used for the syntheses neither changed the final stoichiometry, nor the characteristic

thermogravimetric decomposition in three main steps; however, the solids precipitated from water solutions systematically resulted thermally less stable with respect to those precipitated from ethanolic solutions, sometimes even 150°C less stable. Fig. 5 presents the thermogravimetric curves of the $[\text{Ni}(\text{adr})_6](\text{NO}_3)_2$ complexes precipitated from ethanolic (a) or water (b) solutions. This behaviour could be attributed to the different polarity of the solvents used in the syntheses, with a higher stability of the complexes in water solution than in the ethanolic solution. This means an opposite trend in the solid state, with the solids obtained from ethanolic solutions being thermally more stable than those obtained from aqueous solutions.

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