

Research Article

Complex Formation in a Liquid-Liquid Extraction System Containing Cobalt(II), 4-(2-Pyridylazo)resorcinol, and Nitron

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Received 12 December 2012; Revised 23 February 2013; Accepted 24 February 2013

Academic Editor: Concepción López

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Complex formation and liquid-liquid extraction were studied in a system containing cobalt(II), 4-(2-pyridylazo)resorcinol (PAR), 1,4-diphenyl-3-(phenylamino)-1H-1,2,4-triazole (Nitron, Nt), water, and chloroform. The effect of some experimental parameters (pH, shaking time, concentration of PAR, and concentration of Nt) was systematically investigated, and the optimum conditions for cobalt extraction as an ion-association complex, $(\text{NtH}^+)[\text{Co}^{3+}(\text{PAR})_2]$, were found. The following key equilibrium constants were calculated: constant of association ($\text{Log}\beta = 4.77 \pm 0.06$), constant of distribution ($\text{Log}K_D = 1.34 \pm 0.01$), and constant of extraction ($\text{Log}K_{\text{ex}} = 6.11 \pm 0.07$). Beer's law was obeyed for Co concentrations up to $1.7 \mu\text{g mL}^{-1}$ with a molar absorptivity of $6.0 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ at $\lambda_{\text{max}} = 520 \text{ nm}$. Some additional characteristics, such as limit of detection, limit of quantification, and Sandell's sensitivity, were estimated as well.

1. Introduction

Cobalt is a transition metal which plays an essential role in industry and all living organisms. Its main applications are in the production of special steels and alloys, permanent magnets, cutting tools, batteries, catalysts, pigments for enamels and glass, and dryers for oil, paints, and varnishes. In biological systems cobalt acts as an active nutrient and an active center of coenzymes called cobalamines. The most important representative of this class of compounds is vitamin B-12: a key substance, which is normally involved in the metabolism of every cell of the human body, especially affecting DNA synthesis and neurologic function [1]. Cobalt deficiency (and hence vitamin B-12 deficiency) can lead to a wide spectrum of hematologic, neuropsychiatric, and cardiovascular disorders. On the other hand, cobalt can be toxic when consumed in excessive quantities [2, 3]. That is why its content in various samples is monitored, despite the fact that the existing methods for cobalt determination are not enough sensitive or cost effective [4–7].

4-(2-Pyridylazo)resorcinol (PAR) has been proved to be one of the most important reagents for cobalt separation, preconcentration and determination [6–26]. PAR forms with Co(II) intensively colored anionic chelates, $[\text{Co}^{2+}(\text{PAR})_2]^{2-}$ or $[\text{Co}^{3+}(\text{PAR})_2]^-$, which can readily react with bulky organic compounds [20–36] to give ternary complexes with good extraction behavior and analytical potential. In the present paper, we investigated the complex formation in a liquid-liquid extraction system containing Co(II), PAR, and Nitron (Nt). Nt (Figure 1) is a low-cost and low-toxic analytical reagent that has been commercially available for more than a century; however, some novel aspects of its chemical nature have been recently disclosed [37]. It should be said that extraction systems containing both PAR and Nt have been weakly studied. To the best of our knowledge, the only reported investigations in this field concern vanadium(V) extraction and spectrophotometric determination [38].

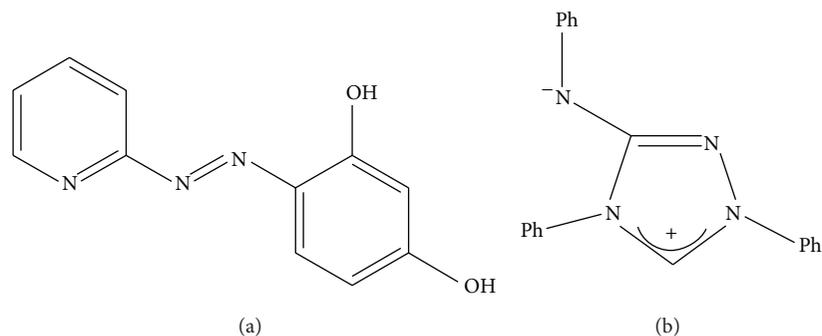


FIGURE 1: Reagents in the present study, (a) 4-(2-pyridylazo)resorcinol (PAR), (b) 1,4-diphenyl-3-(phenylamino)-1H-1,2,4-triazole (Nitron, Nt).

2. Experimental

2.1. Reagents and Apparatus

- (i) $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ (ReagentPlus, $\geq 99\%$, Sigma-Aldrich), 1000 mg L^{-1} stock aqueous solution. Working solutions ($C_{\text{Co}} = 1.7 \times 10^{-4} \text{ mol L}^{-1}$) were prepared by dilution.
- (ii) PAR (96%, Sigma-Aldrich) dissolved in slightly alkalinized distilled water, $2 \times 10^{-3} \text{ mol L}^{-1}$.
- (iii) Nitron ($\geq 97\%$, Fluka), $3.5 \times 10^{-4} \text{ mol L}^{-1}$ chloroform solution freshly prepared each day.
- (iv) Acetate buffer solution, prepared by mixing of 2 mol L^{-1} aqueous solutions of CH_3COOH and NH_4OH . The resulting pH was checked by HI 83140 pH meter (Italy).
- (v) Chloroform (additionally distilled).
- (vi) Ultrospec 3300 pro UV/visible spectrophotometer (Amersham Biosciences), equipped with 10 mm path-length cells.

2.2. Procedure for Establishing the Optimum Operating Conditions. Aliquots of Co(II) solution, PAR solution (up to 1.4 mL), and buffer solution (5 mL; pH ranging from 3.0 to 6.2) were introduced into 250 mL separatory funnels. The resulting solutions were diluted with distilled water to a total volume of 10 mL. Appropriate amounts of Nt solution and chloroform were added in a total volume of 10 mL. Then the funnels were shaken for a fixed time (up to 5.0 min). A portion of the organic extract was filtered through a filter paper (to prevent the opportunity of water droplets transfer) into a cell and the absorbance read against a blank. The blank extraction was performed at the same manner, but in the absence of Co.

2.3. Procedure for Determination of the Distribution Constant. The distribution constant K_D was found from the ratio $K_D = A_1/(A_2 - A_1)$, where A_1 and A_2 are the absorbances (measured against blanks) obtained after a single and double extraction, respectively. The single extraction and the first stage of the double extraction were performed

TABLE 1: Optimum conditions and analytical characteristics of the Co(II)-PAR-Nt-water-chloroform system.

Optimum conditions	Analytical characteristics
Wavelength: 520 nm	Molar absorptivity: $\epsilon = 6.0 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$
pH: 5.3 (acetate buffer)	Beer's law range: up to $1.7 \mu\text{g mL}^{-1}$
$C_{\text{PAR}}: 1.0 \times 10^{-4} \text{ mol L}^{-1}$	Limit of detection: $0.06 \mu\text{g mL}^{-1}$
$C_{\text{Nt}}: 3.0 \times 10^{-4} \text{ mol L}^{-1}$	Limit of quantification: $0.20 \mu\text{g mL}^{-1}$
Shaking time: 15–20 sec	Sandell's sensitivity: 0.99 ng cm^{-2}

under the optimum extraction-spectrophotometric conditions (Table 1). The organic layers were transferred into 25 mL calibrated flasks and the flask for the single extraction was brought to volume with Nt solution. The second stage of the double extraction was performed by adding another 10 mL portion of the Nt solution to the aqueous phase, which remained after the first stage. After shaking, the organic layer was added to the one obtained after the first stage and the volume was brought to the mark with Nt solution. Before the spectrophotometric measurement, the calibrated flasks were shaken for homogenization.

3. Results and Discussion

3.1. Absorption Spectra. Spectra of the extracted ternary Co-PAR-Nt complex and the blank are shown in Figure 2. A maximum is recorded at 520 nm, where the blank absorbs insignificantly. It is shifted to 10 nm as compared to the maximum of the binary Co-PAR chelate existing in aqueous medium (in the pH interval from 3.5 to 10): 510 nm [9, 27, 29, 31, 39]. The observed bathochromic effect is small and gives us grounds to suggest the formation of a ternary compound of the ion-association type.

3.2. Effect of pH. Results showed that the optimal pH for the extraction of Co with PAR and Nt is 5.2–5.4 (Figure 3). A buffer solution with a concentration of 2 mol L^{-1} was applied to control pH. The use of 0.25–5 mL of the buffer solution per 10 mL (final aqueous solution) was found to give a constant

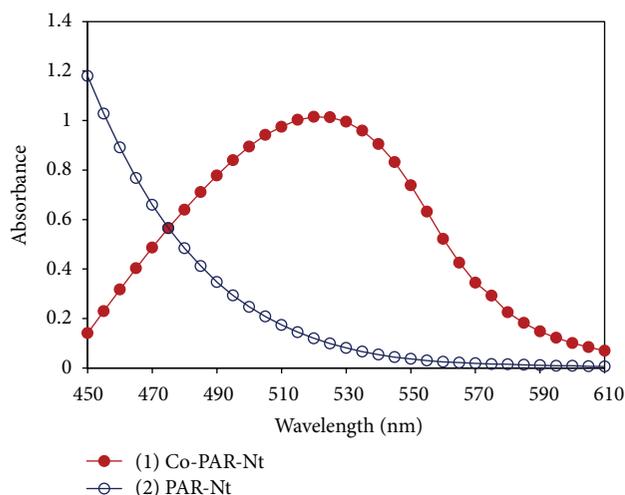


FIGURE 2: Absorption spectra of the ternary Co-PAR-Nt complex and the blank (PAR-Nt) in chloroform. $C_{Co} = 1.7 \times 10^{-5} \text{ mol L}^{-1}$, $C_{PAR} = 1.4 \times 10^{-4} \text{ mol L}^{-1}$, $C_{Nt} = 3.5 \times 10^{-4} \text{ mol L}^{-1}$, and $\text{pH} = 5.3$, $l = 1 \text{ cm}$.

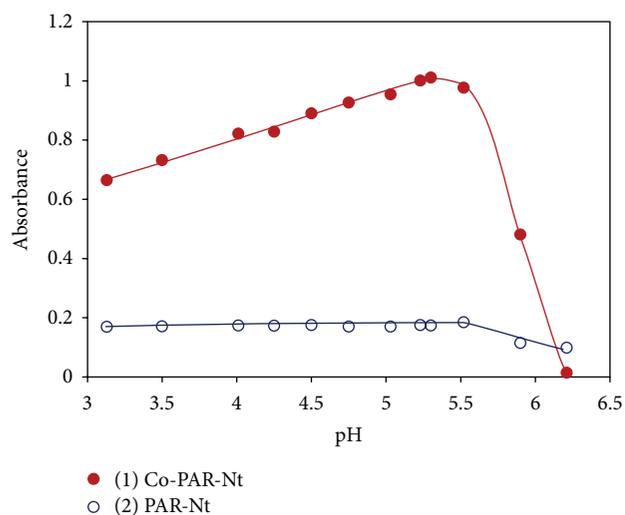


FIGURE 3: Absorbance of Co-PAR-Nt extracts against blank (line 1) and blank against chloroform (line 2) versus pH of the aqueous phase plots. $C_{Co} = 1.7 \times 10^{-5} \text{ mol L}^{-1}$, $C_{PAR} = 1.4 \times 10^{-4} \text{ mol L}^{-1}$, $C_{Nt} = 3.5 \times 10^{-4} \text{ mol L}^{-1}$, $\lambda = 520 \text{ nm}$, and $l = 1 \text{ cm}$.

absorbance. All further experiments were carried out with 5 mL buffer solution with $\text{pH} = 5.2\text{--}5.3$.

3.3. Effect of Reagents' Concentrations. The effect of PAR and Nt concentrations on the absorbance is shown in Figure 4. For up to $1.7 \mu\text{g mL}^{-1}$ of Co, the use of about 0.5 mL of $2.0 \times 10^{-3} \text{ mol L}^{-1}$ PAR and 8.5 mL of $3.5 \times 10^{-4} \text{ mol L}^{-1}$ Nt was found to be sufficient for a complete cobalt extraction.

3.4. Effect of Shaking Time. The extraction equilibrium is reached for a short shaking time (about 5 seconds). It was found that a shaking time longer than 1 min can bring about to a slight decrease (5-6%) of the absorbance values. To

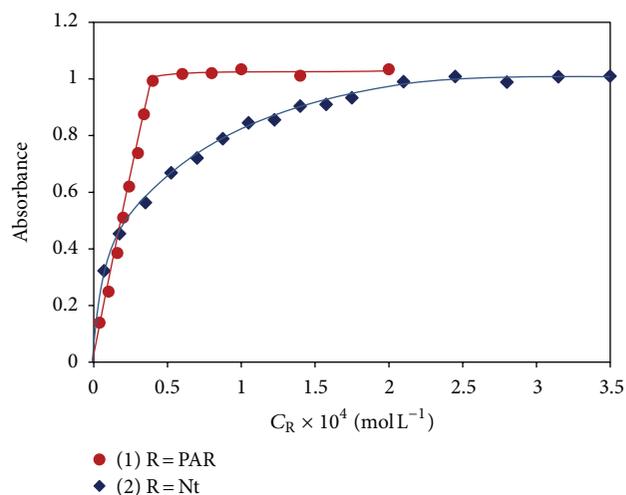


FIGURE 4: Absorbance of the extracted ternary complex versus concentration of the PAR (curve 1) and Nt (curve 2) plots. (1) $C_{Co} = 1.7 \times 10^{-5} \text{ mol L}^{-1}$, $C_{Nt} = 3.5 \times 10^{-4} \text{ mol L}^{-1}$, $\lambda = 520 \text{ nm}$, and $l = 1 \text{ cm}$. (2) $C_{Co} = 1.7 \times 10^{-5} \text{ mol L}^{-1}$, $C_{PAR} = 1.4 \times 10^{-4} \text{ mol L}^{-1}$, $\lambda = 520 \text{ nm}$, and $l = 1 \text{ cm}$.

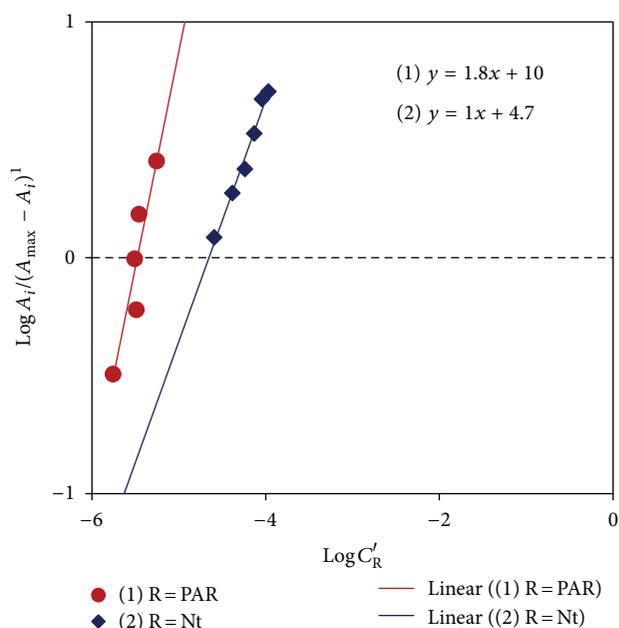


FIGURE 5: Determination of the PAR-to-Co (1) and Nt-to-Co (2) molar ratios by the mobile equilibrium method. (1) $C_{Co} = 1.7 \times 10^{-5} \text{ mol L}^{-1}$, $C_{Nt} = 3.5 \times 10^{-4} \text{ mol L}^{-1}$, $\text{pH} = 5.3$, $\lambda = 520 \text{ nm}$, and $l = 1 \text{ cm}$. (2) $C_{Co} = 1.7 \times 10^{-5} \text{ mol L}^{-1}$, $C_{PAR} = 1.0 \times 10^{-4} \text{ mol L}^{-1}$, $\text{pH} = 5.3$, $\lambda = 520 \text{ nm}$, and $l = 1 \text{ cm}$.

avoid this disadvantage and to guarantee complete transfer of the complex into organic phase, even under nonoptimum conditions, the authors extracted in their experiments for 15–20 seconds.

3.5. Composition of the Complex and Suggested Formula. The molar PAR-to-Co(II) and Nt-to-Co(II) ratios were determined by the mobile equilibrium method [40] (Figure 5), molar ratio method [43] (see Figure 4), and the

TABLE 2: Calculated values of Log β , Log K_D , Log K_{ex} , and R%.

Equilibrium	Equilibrium constant	Value
(1)	$\beta = \frac{[(\text{NtH})[\text{Co}(\text{PAR})_2]]}{[\text{NtH}^+] \times [[\text{Co}(\text{PAR})_2]^-]}$	Log $\beta = 4.7 \pm 0.3^a$ Log $\beta = 4.77 \pm 0.06^b$ Log $\beta = 4.9 \pm 0.1^c$
(2)	$K_D = \frac{[(\text{NtH})[\text{Co}(\text{PAR})_2]_{\text{org}}]}{[(\text{NtH})[\text{Co}(\text{PAR})_2]_{\text{aq}}]}$	Log $K_D = 1.34 \pm 0.01$
(3)	$K_{ex} = \frac{[(\text{NtH})[\text{Co}(\text{PAR})_2]_{\text{org}}]}{[\text{NtH}^+]_{\text{aq}} \times [[\text{Co}(\text{PAR})_2]^-]_{\text{aq}}]}$	Log $K_{ex} = 6.11 \pm 0.07^d$

^a Calculated by the mobile equilibrium method [40].

^b Calculated by the Holme-Langmihr method [41].

^c Calculated by the Harvey-Manning method [42].

^d Calculated by the formula $K_{ex} = K_D \times \beta$, where β is determined by the Holme-Langmihr method.

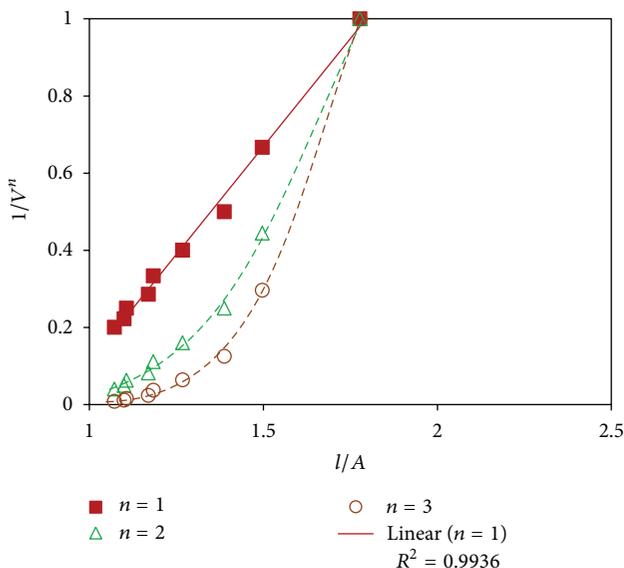
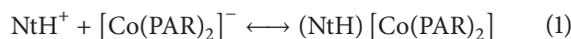


FIGURE 6: Determination of the Nt-to-Co molar ratio by the method of Asmus. $C_{\text{Co}} = 1.7 \times 10^{-5} \text{ mol L}^{-1}$, $C_{\text{PAR}} = 1.0 \times 10^{-4} \text{ mol L}^{-1}$, $\text{pH} = 5.3$, $\lambda = 520 \text{ nm}$, and $l = 1 \text{ cm}$.

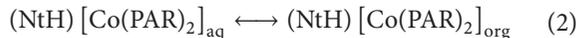
method of Asmus [44] (Figure 6). The results showed that the ternary complex has a composition of 1:2:1 (Co: PAR: Nt). Having in mind the obtained molar ratios and several reports, which convincingly demonstrate that the labile Co(II)-PAR complex can be easily oxidized to an inert Co(III)-PAR complex, $[\text{Co}^{3+}(\text{PAR})_2]^-$, by the atmospheric oxygen [13, 26, 29, 32, 33, 36, 45], we suggest the following formula of the extracted ternary species: $(\text{NtH})^+[\text{Co}^{3+}(\text{PAR})_2]^-$. In this formula, PAR is in deprotonated form (PAR^{2-}), while Nt is in protonated form (NtH^+). The mentioned formula and the known properties of PAR [45–47] and Nt [48] fit well to the observed pH curve of the ternary complex presented in Figure 3: (1) at pH values lower than pH_{opt} PAR is hardly possible to be in its PAR^{2-} form; (2) at pH values higher than pH_{opt} Nt is hardly possible to be in its NtH^+ form. The right part of the pH curve has a steeper slope, because the limitation 2 is more strictly.

3.6. Equilibrium Constants and Recovery. Several equilibrium processes should be taken into account for the system of $[\text{Co}(\text{PAR})_2]^-$, NtH^+ , water, and chloroform.

(i) Formation of ion-association complex in the aqueous phase:



(ii) Distribution of the complex between the aqueous and the organic phase:



(iii) Extraction from water into chloroform:



The equilibrium constants describing these equations and the obtained values are shown in Table 2. The association constant β was determined by several independent methods: Holme-Langmihr method [41], Harvey-Manning method [42], and mobile equilibrium method [40] (Figure 5, straight line 2). The distribution constant K_D was calculated from the absorption values obtained after single and double extraction as described above. The extraction constant K_{ex} was calculated by the formula $K_{ex} = K_D \times \beta$. The recovery factor R was estimated by the dependence $R\% = 100 K_D / (K_D + 1)$ and the following value was obtained $R = 95.7\%$. All experiments were performed at room temperature of $\sim 22^\circ\text{C}$ and the calculations were carried out at a probability of 95%.

3.7. Beer's Law, Molar Absorptivity, and other Analytical Characteristics. The range of adherence to Beer's law was studied at the optimum conditions (Table 1). The linearity is observed up to $1.7 \mu\text{g mL}^{-1}$ of Co with a correlation coefficient of 0.9995. The obtained straight line equation is $Y = 0.973X + 0.014$. The molar absorptivity was calculated to be $6.0 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$. This value could compete successfully with the ones obtained for similar PAR-containing complexes (Table 3). The limit of detection (LOD) and limit of quantification (LOQ) were estimated at 3 times and 10 times standard deviation of the intercept divided by the slope. Sandell's sensitivity was calculated as well. The values of the above-mentioned characteristics are included in Table 1.

4. Conclusions

Cobalt(II) forms well chloroform-extractable ternary complex with 4-(2-pyridylazo)resorcinol and Nitron. The complex could be regarded as an ion associate between an

TABLE 3: Spectral characteristics of some extracted in organic solvents Co-PAR complexes*.

Additional reagent(s)	Organic solvent	Molar absorptivity, $L mol^{-1} cm^{-1}$	λ_{max} , nm	Ref.
Xylomethazoline hydrochloride	Chloroform	4.2×10^4	535	[24]
Diphenylguanidine	Chloroform	5.0×10^4	520–530	[27]
Triphenyltetrazolium chloride	Chloroform	5.0×10^4	515	[36]
Iodonitrotetrazolium chloride	Chloroform	5.2×10^4	515	[36]
Zephiramine	Chloroform	5.8×10^4	520	[28]
Tetradecyl-dimethylbenzyl-ammonium chloride + EDTA	Chloroform	5.9×10^4	520	[35]
Dicyclohexyl-18-crown-6	1,2-dichloroethane	6.0×10^4	515	[26]
Tetraphenylarsonium chloride	Chloroform	$(6.0-6.4) \times 10^4$	520	[29]
Tetraphenylphosphonium chloride	Chloroform	$(6.0-6.4) \times 10^4$	520	[29]
Nitron	Chloroform	6.0×10^4	520	This work

*The molar absorptivity of the binary cobalt-PAR complex in aqueous medium is $\epsilon_{510} = 5.6 \times 10^4 L mol^{-1} cm^{-1}$ [39].

intensively colored anion, $[Co(PAR)_2]^-$, in which cobalt is in +3 oxidation state, and a bulky hydrophobic cation (protonated Nitron, NtH^+). The following equilibrium constants and analytical characteristics were determined: constant of extraction, constant of association, constant of distribution, recovery factor, molar absorptivity, Sandell's sensitivity, limit of detection, and limit of quantification. The obtained values show that the studied extraction system in the present work could compete successfully with many similar systems used for cobalt determination.

Acknowledgment

The authors would like to thank the Research Fund of the Plovdiv University for its long-time support.

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