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SULFITOAMINE COMPLEXES OF COBALT(III)

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Monosulfito and bis(hydrogensulfito) cobalt(III) complexes were prepared using sodium sulfite and sodium metabisulfite salts respectively. The two types of products showed different and characterizing patterns of IR and UV-visible spectra. They both contain Co—SO₃ linkages and the sulfite groups have similar or different site symmetries in the same compound.

Key words: Sulfite; hydrogensulfite; amine; cobalt(III); complexes; IR spectra; synthesis.

INTRODUCTION

Transition metal sulfites and SO₂ are of the main pollutants in the atmosphere. Recent epidemiology and animal toxicology studies indicate that reactions between SO₂ and metal containing aerosols result in the formation of respiratory irritants. Oxidation of S(IV) to S(VI) in aqueous solution is generally known to be catalyzed by traces of transition metal ions such as Mn²⁺/Mn³⁺, Fe²⁺/Fe³⁺, Co²⁺/Co³⁺, and Cu²⁺.^{1–6} This reaction represents a viable pathway for the oxidation of dissolved SO₂ to sulfate in atmospheric water droplets during the acid-rain process.

Van Eldik *et al.* and Harris *et al.*^{7–14} have studied the kinetics of formation and oxidation of sulfito complexes using Co(III) complexes. They found that various ammine and amine aquo cobalt(III) complex ions react with aqueous sulfur dioxide by direct addition to yield oxygen-bonded sulfito complexes. These O-bonded products are unstable and either isomerize to a stable S-bonded form or undergo internal redox. Thus [Co(NH₃)OSO₂]⁺ very rapidly undergoes intra-molecular electron transfer at high pH values, 3.4 < pH < 6.7, and produces Co(aq)²⁺ and SO₄²⁻ in a 2:1 molar ratio.⁷ However, the stability of the O-bonded sulfito complex strongly depends on the nature of the amine ligands. For example, in the case of tetraethylenepentamine complex, the O-bonded species was found to be redox inert.

Differentiation between different types of SO₃ linkage in sulfitoamine cobalt(III) complexes and also between mono- and disulfito products have been discussed by previous researchers.^{15–20} In this work, we aimed to further investigate these differentiations by preparing new sulfitoamine cobalt(III) complexes using both Na₂SO₃ and Na₂S₂O₅ as different sources of sulfite ions.

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EXPERIMENTAL

Materials. Sodium sulfite, sodium metabisulfite, cobalt chloride hexahydrate, cobalt sulfate heptahydrate, ethylenediamine and (1,2-diaminopropane) were Merck products. Other chemicals used were all reagent grade.

Preparation of the start complexes. The following start complexes were prepared: trans-[Co(1,2pn)₂Cl₂]Cl,²¹ trans-[Co(1,2pn)₂Cl₂]ClO₄ · ½H₂O,²¹ trans-[Co(1,2pn)(en)Cl₂]ClO₄ · H₂O²¹ and cis-[Co(en)₂(NH₃)Br]Br₂ · H₂O,²² [1,2pn = 1,2-diaminopropane and en = ethylenediamine]. The chemical analysis of these complexes was satisfactory.

Preparation of chlorosulfitobis(1,2-diaminopropane)cobalt(III) monohydrate, [Co(1,2pn)₂(SO₃)Cl] · H₂O. A solution of 0.4 g (3.2 mmol) sodium sulfite in 2 ml water was added to a solution of trans-dichlorobis(1,2-diaminopropane) cobalt(III) chloride, 1 g (3.2 mmol), in 3 ml water. On gentle heating red brown crystals appeared. The solution was cooled then filtered. The product was crystallized from minimum amount of water, filtered and washed with methanol, ether and then air-dried. The yield was 0.67 g (61%), m.p. 230°C (decomp.). Analysis for [Co(C₃H₁₀N₂)₂(SO₃)Cl] · H₂O. Calcd.: C, 21.2; H, 6.5; N, 16.4; S, 9.4; Cl, 10.4%. Found: C, 20.8; H, 6.2; N, 16.1; S, 9.0; Cl, 10.8%.

Preparation of chlorosulfitobis(1,2-diaminopropane)cobalt(III) tetrahydrate-sodium chloride, [Co(1,2pn)₂(SO₃)Cl] · 4H₂O · NaCl. Trans-dichlorobis(1,2-diaminopropane)cobalt(III) perchlorate hemihydrate, 0.3 g (0.8 mmol), and sodium sulfite, 0.1 g (0.8 mmol), were dissolved in a minimum amount of hot water. The resultant solution was heated to 60°C for several minutes, and stirred for half an hour. The pH of the solution was acidic (5.4). Methanol (20 ml) was added, a brown precipitate was formed and obtained by filtration. The product was crystallized from the minimum amount of water, filtered and washed with methanol, ether then air-dried. The yield was 0.2 g (60%), m.p. 245°C (decomp.). Analysis for [Co(C₃H₁₀N₂)₂(SO₃)Cl] · 4H₂O · NaCl. Calcd.: Co, 13.0; Na, 5.1; C, 15.9; H, 6.2; N, 12.4; S, 7.1; Cl, 15.7%. Found: Co, 12.6; Na, 6.0; C, 15.9; H, 5.8; N, 12.1; S, 7.5; Cl, 14.9%.

Preparation of chlorosulfito(1,2-diaminoethane)(1,2-diaminopropane)cobalt(III)-monohydrate-sodium chloride, [Co(1,2pn)(en)(SO₃)Cl] · H₂O · NaCl. The procedure followed was the same as the previous preparation. Trans-dichloro(1,2-diaminoethane)(1,2-diaminopropane)cobalt(III) monohydrate, 0.3 g (0.8 mmol), and sodium sulfite, 0.1 g (0.8 mmol), were used. A brick red precipitate was obtained. The yield was 0.24 g (75%), m.p. 240°C (decomp.). Analysis for [Co(C₂H₁₀N₂)(C₂H₈N₂)(SO₃)Cl] · H₂O · NaCl. Calcd.: C, 15.6; H, 5.2; N, 14.5; Cl, 18.4; S, 8.3; Na, 6.0%. Found: C, 15.2; H, 5.3; N, 14.6; Cl, 19.0; S, 8.2; Na, 6.4%.

Preparation of bromosulfitobis(1,2-diaminoethane)cobalt(III) dihydrate, [Co(en)₂(SO₃)Br] · 2H₂O. The reaction of cis-bromoamminebis(1,2-diaminoethane)cobalt(III) bromide monohydrate and sodium sulfite was carried out using two different ratios of the starting materials. Although the products obtained have similar molecular formula, their IR spectra were different as will be discussed later.

1. Reaction of cis-[Co(en)₂(NH₃)Br]Br₂ · H₂O and Na₂SO₃, molar ratio 2:1. The start cobalt complex, 1 g (2.2 mmol), and sodium sulfite, 0.14 g (1.1 mmol), were dissolved in the minimum amount of warm water and the resultant deep brown solution was heated to 60°C for 10 minutes. A deep brown oil was obtained by the addition of ethanol followed by ether. The oil was washed several times with ether where it turned to a deep brown solid. The crude hygroscopic product was washed with ethanol and ether, air-dried then left in a desiccator over conc. H₂SO₄ for one day. The yield was 0.2 g (48%), m.p. 245°C (decomp.). Analysis for [Co(C₂H₈N₂)₂(SO₃)Br] · 2H₂O (I). Calcd.: C, 12.8; H, 5.3; N, 14.9; Br, 21.3; S, 8.5%. Found: C, 12.7; H, 5.4; N, 14.5; Br, 20.7; S, 7.8%.

2. Reaction of cis-[Co(en)₂(NH₃)Br]Br₂ · H₂O and Na₂SO₃, molar ratio 1:1. The start cobalt(III) complex, 0.5 g (1.1 mmol), and sodium sulfite, 0.14 g (1.1 mmol), were treated as in the previous preparation. A red brown precipitate was obtained by the addition of ethanol. The yield was 0.3 g (72%), m.p. 245°C (decomp.). Analysis for [Co(C₂H₈N₂)₂(SO₃)Br] · 2H₂O (II). Calcd.: C, 12.8; H, 5.3; N, 14.9; Br, 21.3; S, 8.5%. Found: C, 12.6; H, 5.5; N, 14.5; Br, 21.6; S, 8.6%.

Preparation of bis(hydrogensulfito)(1,2-diaminoethane)(1,2-diaminopropane)cobalt(III)-sulfite trihydrate-sodium sulfite, [Co(1,2pn)(en)(HSO₃)₂](SO₃)_{1/2} · 3H₂O · ½Na₂SO₃. Trans-dichloro(1,2-diaminoethane)(1,2-diaminopropane)cobalt(III) perchlorate monohydrate, 0.5 g (1.3 mmol), and sodium metabisulfite, 0.75 g (3.9 mmol), were dissolved in the least amount of water. The resultant

solution was heated to 70°C for several minutes, and then stirred for half an hour. The pH of the solution was acidic (5.0). Methanol (20 ml) was then added. A yellow precipitate was formed and obtained by filtration. The product was crystallized from the minimum amount of water, filtered, washed with methanol then ether. The yield was 0.4 g (60%), m.p. > 240°C (changes its colour to pale brown at 170°C). Analysis for $[\text{Co}(\text{C}_3\text{H}_{10}\text{N}_2)(\text{C}_2\text{H}_8\text{N}_2)(\text{HSO}_3)_2](\text{SO}_3)_{1/2} \cdot 3\text{H}_2\text{O} \cdot \frac{1}{2}\text{Na}_2\text{SO}_3$. Calcd.: C, 11.7; H, 5.1; N, 10.9; S, 18.7; Na, 4.5. Found: C, 11.6; H, 5.0; N, 11.4; S, 18.0; Na, 4.6.

Trials to prepare other disulfite complexes by reacting the starting complexes with $\text{Na}_2\text{S}_2\text{O}_5$, 1:3 molar ratio, or with Na_2SO_3 , 1:2 molar ratio, yielded yellow precipitates characteristic of the disulfite products.¹⁵ These products have similar IR and UV-visible spectra but are different from those of the monosulfite products. The previous prepared mixed ethylenediamine-1,2-propanediamine was the only complex obtained in a pure state. The rest of these products are usually contaminated with excess Na_2SO_3 and their purification is difficult due to solubility problems. Both the product and excess Na_2SO_3 are soluble in water and DMF- H_2O mixture (1:1 by volume) and both precipitate together by the addition of methanol. Crystallization from these solutions yielded yellow crystals of the products contaminated with white Na_2SO_3 crystals. We did not attempt to separate them by other means.

ANALYSIS AND SPECTRA

Chemical analysis was performed at the Fine Chemical Analysis Center, Cairo University, Giza, Egypt. The IR spectra ($400\text{--}4000\text{ cm}^{-1}$) of the complexes on KBr discs were recorded on a Perkin-Elmer spectrometer 598. Visible and UV spectra of aqueous solutions of the complexes were recorded on a Varian S, DMS 100S UV-visible spectrophotometer. Conductivity measurements were carried out using a conductivity meter, Mod. LBR 40 A, West Germany and checked on another conductivity meter, Kent Eil 5003, Mod. MC-1, Mark V, Electrolytic conductivity measuring set, England.

RESULTS AND DISCUSSION

All the prepared complexes are soluble in water and conduct electricity. Their conductivity values are shown in Table I and indicate that the monosulfite products are 1:1 electrolytes and the disulfite product is a 1:2 electrolyte. The conductivity of the monosulfite products indicate that the coordinated halide ion has exchanged with a water molecule. Baldwin has obtained a similar product

TABLE I
UV-Visible absorption spectra and conductivity of sulfitoamine Cobalt(III) complexes

Complex	UV-Visible λ_{max} , nm	Spectra ϵ , $\text{M}^{-1}\text{ cm}^{-1}$	Conductivity $\text{ohm}^{-1}\text{ cm}^2\text{ mol}^{-1}$ at 25°C
A. Monosulfite products			
$[\text{Co}(1, 2\text{pn})_2\text{SO}_3\text{Cl}] \cdot \text{H}_2\text{O}$	470, 287, 234	106, 4758, 974	120
$[\text{Co}(1, 2\text{pn})_2(\text{SO}_3)\text{Cl}] \cdot 4\text{H}_2\text{O} \cdot \text{NaCl}$	465, 286, 245	70, 3956, 268	210
$[\text{Co}(1, 2\text{pn})(\text{en})(\text{SO}_3)\text{Cl}] \cdot \text{H}_2\text{O} \cdot \text{NaCl}$	467, 287, 244	112, 4642, 528	200
$[\text{Co}(\text{en})_2(\text{SO}_3)\text{Br}] \cdot 2\text{H}_2\text{O}$	465, 287, 244	94, 4642, 528	140
B. Disulfite products			
$[\text{Co}(1, 2\text{pn})(\text{en})(\text{HSO}_3)_2](\text{SO}_3)_{1/2} \cdot 3\text{H}_2\text{O} \cdot \frac{1}{2}\text{Na}_2\text{SO}_3$	438, 294, 266	137, 3450, 3420	300

TABLE II
Infrared frequencies (cm^{-1}) of bands due to sulfito groups in sulfitoamine cobalt(III) complexes

Complex	Stretching Vibrations				Bending vibrations			
A. Monosulfito products:								
1. $[\text{Co}(\text{l}, 2\text{pn})_2(\text{SO}_3)\text{Cl}] \cdot \text{H}_2\text{O}$	1165 m, sh	1100 vs, b	1035 s	965 vs	910 s	610 vs, b	510 m	
2. $[\text{Co}(\text{l}, 2\text{pn})_2(\text{SO}_3)\text{Cl}] \cdot 4\text{H}_2\text{O} \cdot \text{NaCl}$	1135 vs	1115 vs, sh	1080 vs, b	975 s, sh	905 s	610 vs, b	510 m	
3. $[\text{Co}(\text{l}, 2\text{pn})(\text{en})(\text{SO}_3)\text{Cl}] \cdot \text{H}_2\text{O} \cdot \text{NaCl}$	1145 vs, b	1145 vs, b	1085 vs, b	975 m	910 vs, b	615 s, b	515 m	
4. $[\text{Co}(\text{en})_2(\text{SO}_3)\text{Br}] \cdot 2\text{H}_2\text{O}$ I	1185 s, sh	1155 s, sh	1145 s, b	970 s, sh	905 m	615 m	500 w, b	
II								
	1185 s, sh	1155 s, sh	1105 vs, b	975 s, b	940 m	620 s, b	510 m	
B. Disulfito products:								
$[\text{Co}(\text{l}, 2\text{pn})(\text{en})(\text{HSO}_3)_2](\text{SO}_3)_{1/2} \cdot 3\text{H}_2\text{O} \cdot \frac{1}{2}\text{Na}_2\text{SO}_3$	1170 s, sh	1110 s, sh	1095 vs, b	1005 vs	950 s	650 s	520 w	

$[\text{Co}(\text{en}_2(\text{SO}_3)\text{Cl}) \cdot \text{H}_2\text{O}]$.¹⁵ She based this formula on the fact that the IR spectra of the hydrated and anhydrous compounds were similar. Also, the aqueous solution of the compound conducted electricity and is shown to be 1:1 electrolyte. Some of the products were coprecipitated with NaCl or Na_2SO_3 leading to the increase of their conductance. Similar coprecipitation occurred in the case of the reaction of $[\text{Co}(\text{tren})(\text{CO}_3)]\text{ClO}_4$, $[\text{Co}(\text{tren})(\text{OH}_2)_2](\text{ClO}_4)$ and $[\text{Co}(\text{tren})(\text{OH})_2]\text{Cl}_3$ with $\text{Na}_2\text{S}_2\text{O}_5$, $\text{tren} = 2,2',2''$ -triaminoethylamine. Trials to remove the coprecipitated Na_2SO_3 , NaClO_4 and NaCl salts by several recrystallizations were unsuccessful.¹²

The IR spectra of the sulfito group(s) in four monosulfito and one bis(hydrogensulfito) products are shown in Table II. In the case of monosulfito products four stretching vibrations are usually observed at ~ 1110 , 1040 , 970 , and 910 cm^{-1} . Two bending vibrations are also observed at ~ 615 and 510 cm^{-1} . The corresponding vibrations of the bis(hydrogensulfito) product occur at different frequencies and appear to have a different characterizing pattern. The stretching frequencies of the latter product are at 1095 , 1030 , 1005 , and 950 cm^{-1} . Two bending vibrations appear over 600 cm^{-1} , at ~ 660 and 620 cm^{-1} , in comparison to only one bending vibration in this region for monosulfito products. A third bending vibration appeared at 520 cm^{-1} . Figures 1 and 2 show the differences in the IR patterns for the mono- and di-sulfito products. The latter figure includes another two disulfito products which did not give satisfactory chemical analysis, due to contamination with excess Na_2SO_3 , but are reproduced here as their spectra resemble the bis(hydrogensulfito) product.

Splitting of the stretching and bending vibrations of the SO_3 group(s) in Co(III) sulfito complexes have been observed by previous authors.¹⁵⁻¹⁷ They differentiated between monodentate S-bonded and chelate O-bonded complexes by the number of the vibrations in their IR spectra. The appearance of three stretching and only one bending vibration $\sim 600\text{ cm}^{-1}$ characterize the former type of linkage. While splitting of the stretching vibrations to more than three bands and the appearance of two bending vibrations, instead of one, is characteristic of the latter linkage. From the kinetic studies on sulfito cobalt(III) complexes,⁷⁻¹⁴ it was shown that the stable forms of these complexes contain always S-bonded sulfito group(s). UV-visible spectra were used to differentiate between the O-bonded intermediates and the S-bonded products. A $\text{Co}-\text{OS}(\text{O})_2$ species has absorption peaks at ~ 510 – 520 nm ($\epsilon \sim 80$ – 150) and ~ 325 – 330 nm ($\epsilon \sim 1800$ – 2100), whereas $\text{Co}-\text{SO}_3$ species absorb at ~ 440 – 460 nm ($\epsilon \sim 140$ – 250) and $\sim 280\text{ nm}$ ($\epsilon \sim 16000$ – 19500). The visible spectra of the prepared sulfito complexes, in this work, are shown in Table I and indicate that they are S-bonded too. Accordingly, the observed splitting of the IR vibrations of the SO_3 group cannot be interpreted as due to chelation. It seems more likely that these splittings are due to differences in site symmetries of the sulfite groups in the same compound.

Fortunately, the complex $[\text{Co}(\text{en})_2(\text{SO}_3)\text{Br}] \cdot 2\text{H}_2\text{O}$ was obtained twice, products (I) and (II). Although their chemical analysis was identical, they differed in the number of the main stretching vibrations. The first product shows four vibrations at 1110 , 1045 , 970 , and 905 cm^{-1} , while the second product shows mainly two at 1105 and 975 cm^{-1} . These latter vibrations coincide with the first

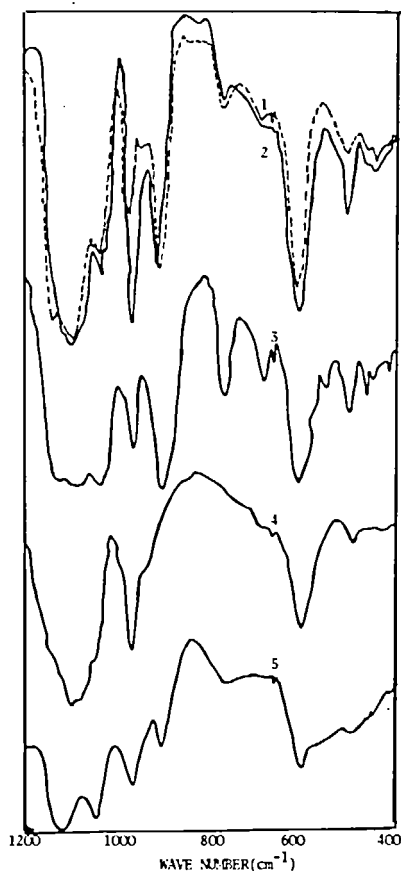


FIGURE 1 Infrared spectra of: 1-[Co(1, 2pn)₂(SO₃)Cl] · 4H₂O · NaCl, 2-[Co(1, 2pn)₂(SO₃)Cl] · H₂O, 3-[Co(1, 2pn)(en)(SO₃)Cl] · H₂O · NaCl, 4-[Co(en)₂(SO₃)Br] · 2H₂O (II) and 5-[Co(en)₂(SO₃)Br] · 2H₂O (I).

and third ones of the first product. Thus, it could be concluded that the sulfito groups in the first product have two different site symmetries, while in the second product they have similar site symmetries due to different crystal packing arrangements.

The IR spectra of the disulfito products differ from those of the monosulfito complexes. Similar observations were reported by previous researchers.¹⁸⁻²⁰ They were able to differentiate between *cis*- and *trans*-coordinated sulfito groups. The *cis*-form shows much more complicated IR spectrum and fewer IR/Raman coincidences than does the *trans*-isomer.

The products of the reactions of Na₂S₂O₅ with *trans*-[Co(1, 2pn)(en)Cl₂]ClO₄ · H₂O and *trans*-[Co(1, 2pn)₂Cl₂]ClO₄ · ½H₂O, molar ratio 3:1, most probably contain *trans*-hydrogensulfito groups. Thus, the splitting observed in the vibrations of the HSO₃ groups is due to the nonequivalence of the S—O bonds. While the two sulfito groups in the reaction of Na₂SO₃ and *cis*-[Co(en)₂(NH₃)Br]Br₂ · H₂O, molar ratio 2:1, is expected to be in the

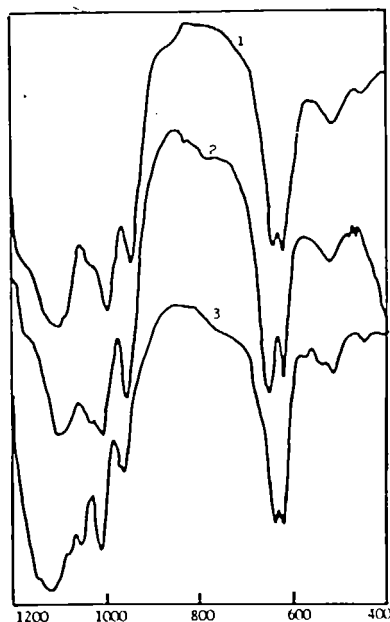


FIGURE 2 Infrared spectra of: 1-[Co(1,2pn)(en)HSO₃)₂](SO₃)_{1/2}·3H₂O·½Na₂SO₃ 2-Product of [Co(1,2pn)₂Cl₂](ClO₄)·H₂O with Na₂S₂O₅ 1:3 3-Product of [Co(en)₂(NH₃)Br]Br₂·H₂O with Na₂SO₃ 1:2.

cis-positions. The splitting in the SO₃ vibrations of the latter product is thus similar to the above mentioned observations on related cis-disulfite products.

The bis(hydrogensulfite) product also contains ionic sulfite groups. The IR spectrum of the SO₃²⁻ ion usually shows a single broad peak at 970 cm⁻¹ due to both the asymmetric and symmetric stretching vibrations fused together. Also, it shows two bending vibrations, symmetric and asymmetric, at 630 and 496 cm⁻¹, respectively. These vibrations are over-lapped with the nearby vibrations of the coordinated hydrogen-sulfite groups, e.g. the band at 970 cm⁻¹ of ionic SO₃²⁻ with the band at 950 cm⁻¹ of the coordinated HSO₃ groups.

The visible-UV spectrum of the disulfite product also differs from those of the monosulfite products. The band due to the transition ¹A_{1g} → ¹T_{1g} occurs at higher energy region, 22800 cm⁻¹ (438 nm), compared to monosulfite products, where the same band occurs at 21500 cm⁻¹ (~465 nm), due to the presence of two sulfite groups in the disulfite product corresponding to only one sulfite group and a halide anion, as ligands, in the monosulfite products. The SO₃ group is thus a strong ligand shifting visible absorption bands to higher energies. The second transition ¹A_{1g} → ¹T_{1g} is not observed in all sulfite complexes as it would be overlapped by a stronger absorption band of the Co—SO₃ species.

The Co—SO₃ species have two absorption bands in the UV region characterized by their high ε values compared to those of d-d transitions of the Co(III) cations. These two bands appear at ~287 and 244 cm⁻¹ in the case of monosulfite products and at 294 and 266 cm⁻¹ in the disulfite product.

Finally, it could be concluded that monosulfito products are all S-bonded with different or similar site symmetries of the SO_3 groups in the same compound. The disulfito products have different and characterizing IR and UV-visible. The latter compounds also contain S-bonded sulfito groups.

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