

A New iso-Amyl Benzothiazolyl Sulfoxide as an Extractant for Palladium and the Crystal Structure of its Palladium (II) Complex

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Abstract: A new iso-amyl benzothiazolyl sulfoxide (ABSО) was synthesized and used in the extraction of Pd(II) from hydrochloric acid media. Pd(II) was extracted quantitatively from 0.1 M HCl with ABSО in benzene (0.5 M). Ammonia solution (2.0 M) could be used as stripping agent. ABSО and Pd(II) form a 2:1 adduct [Pd (ABSО)₂Cl₂] in the extraction. X-ray crystal structure determination revealed PdCl₂(ABSО)₂ is a square-planar complex in which ABSО acts as a neutral unidentate ligand coordinated with palladium(II) via the thiazolyl N atom.

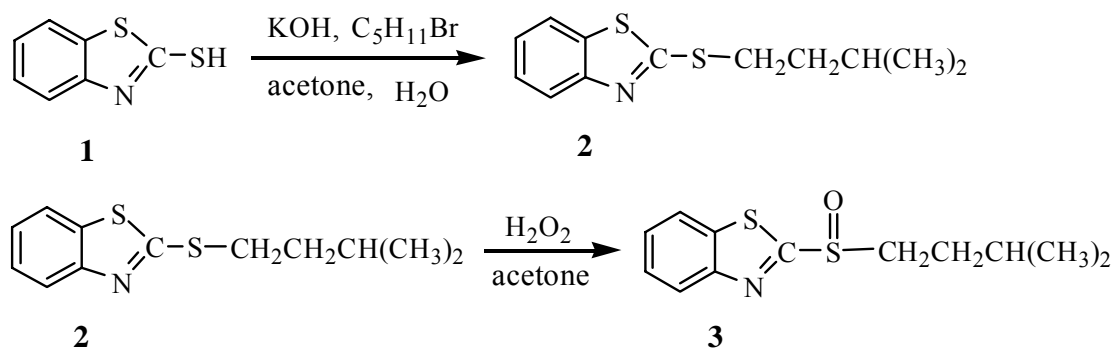
Keywords: Iso-amyl benzothiazolyl sulfoxide; Palladium; Solvent extraction; Crystal structure

Introduction

Palladium is a good catalyst and is widely used in hydrogenation and dehydrogenation reactions. Owing to its corrosion resistance properties and easy alloying, palladium and its alloys are also used in chemical industry, medical devices and jewelry manufacture [1,2]. As Pd(II) can form a number of

complexes that are soluble in organic solvents [3], solvent extraction has become an effective technique in the recovery and separation of palladium from aqueous solutions [4-7]. One coordination chemistry property of Pd(II) is that it prefers to coordinate most strongly with polarizable atoms, a fact that has pushed the development of extractants bearing donor atoms such as sulfur, phosphorus and nitrogen. These ligands are ‘soft’ bases according to the empirical Pearson classification [9]. Sulfoxides are known to be highly selective for extraction of Pd(II), and have been widely used in the extraction of this species [10-12]. So far, most sulfoxides reported for this purpose are petroleum or dialkyl sulfoxides. In this work, a new sulfoxide extractant bearing a heterocyclic substituent, iso-amyl benzothiazolyl sulfoxide (ABSO, **3**), was prepared by the oxidation of the corresponding iso-amyl benzothiazolyl sulfide ether (**2**, Figure 1). Its extraction behavior towards Pd(II) was also investigated and a Pd(II)-ABSO adduct – $[\text{PdCl}_2(\text{ABSO})_2]$ – was obtained in crystal form. The crystal structure of $\text{PdCl}_2(\text{ABSO})_2$ showed that ABSO acts as a neutral unidentate ligand coordinated with Pd(II) via the benzothiazolyl N atom; this is quite different from general Pd(II) dialkyl sulfoxide complexes in which sulfoxides are coordinated with palladium via the O or S atoms of the ligand [13-16].

Figure 1. The synthetic route of iso-amyl benzothiazolyl sulfoxide



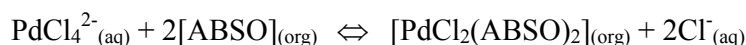
Results and Discussion

Extraction behavior of ABSO towards Pd(II)

Extractions were carried out by shaking equal volumes (10 mL) of the Pd(II) aqueous solution and ABSO dissolved in benzene with the extractant concentration varying from $5 \times 10^{-2} \sim 1.0$ M. It was found the percentage extraction of Pd(II) increases as the extractant concentration increases, and 0.5 M ABSO was needed for quantitative extraction of Pd(II) from a 0.1 M HCl aqueous solution containing 100 mg/L palladium (Figure 2). The effect of HCl concentration on the extraction of Pd(II) is shown in Figure 3. The extraction curve indicated the percentage of extraction of Pd(II) decreased drastically with the increase of HCl concentration. Quantitative extraction of palladium occurred at 0.1 M HCl. Therefore, 0.1 M HCl was adopted in all subsequent experiments. Equilibrium time was determined by measuring the metal content in the aqueous phase as a function of time until the metal concentration in the aqueous solution did not vary. The two phases were shaken for a period ranging from 3 to 30 min. The minimum period of equilibration required for the quantitative extraction of palladium was found to be about 15 min. Palladium loaded in the organic phase was stripped with various stripping agents,

such as HCl, HNO₃, NaOH, NH₃·H₂O and Na₂SO₃ (Table 1). The stripping was observed only with NaOH, NH₃·H₂O and Na₂SO₃ as stripping agents. It was found the stripping was less than 40% when NaOH solution was used as stripping agent. The stripping was quantitative when 2.0 M ammonia solution was used. Hence, 2.0 M ammonia solution can be used as the effective stripping agent.

The ratio of metal ion extractant in the extracted species can be determined by plotting log D (D: distribution ratio) versus log [extractant] at constant pH [17,18]. As can be seen in Figure 4, Plots of log D versus log [ABS O] for the extraction of Pd(II) at 0.1 and 1.0 M HCl yield slopes of 2.13 and 1.91 respectively. This indicates that two ABSO molecules were involved in the extracted Pd(II)-ABS O adduct. Furthermore, we have studied the dependence of Pd(II) extraction upon the acidity. [H⁺] was varied from 0.1 M to 2.0 M while maintaining a constant ionic strength (Cl⁻ = 2.0 M) by adding NaCl. Experimental results showed the variation of [H⁺] did not affect the distribution ratio. This is similar to petroleum sulfoxide and dialkyl sulfoxide cases in the extraction of palladium(II) at low acidity [19-21]. So the extraction of Pd(II) by ABSO may be depicted as:



Since the extraction percentage of Pd (II) decreased drastically with the increasing of hydrochloric acid concentration, while the extraction was independent on acidity, an increase in Cl⁻ concentration should have a negative effect on the extraction of Pd (II). Such a tendency was actually observed by adding NaCl to the extraction system. A plot of logD versus log[Cl⁻] yielded a straight line with a slope of about -2.0 (Figure 5), showing that two Cl⁻ ions were released during the extraction of Pd (II).

Figure 2. Effect of extractant concentration on the percentage extraction of palladium. [Pd(II)] = 100 mg·L⁻¹; ■: 0.1 M HCl; ▲: 2.0 M HCl.

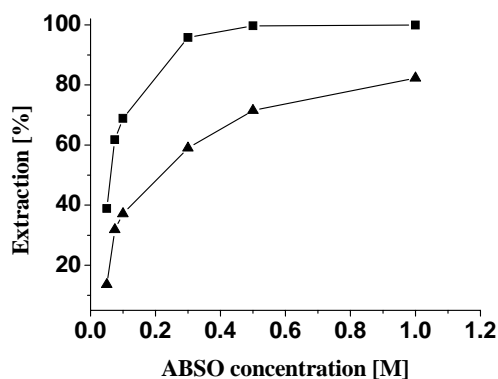


Figure 3. Effect of HCl concentration on the percentage extraction of palladium. [Pd(II)] = 100 mg·L⁻¹; Organic phase: 0.5 M ABSO in benzene.

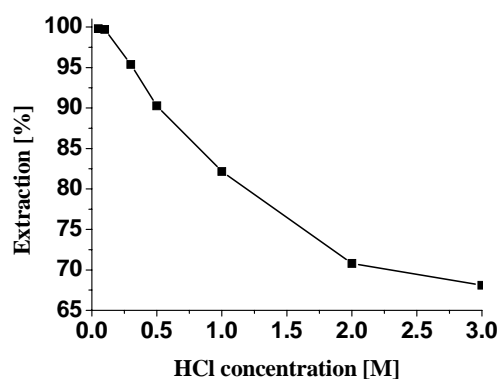
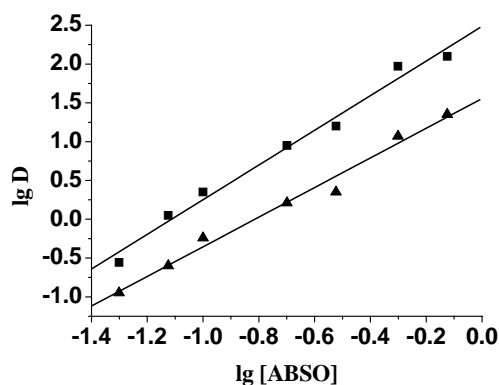
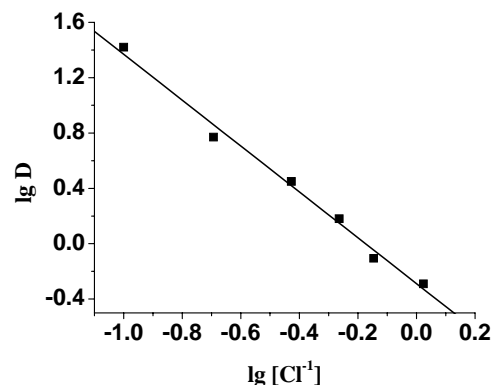


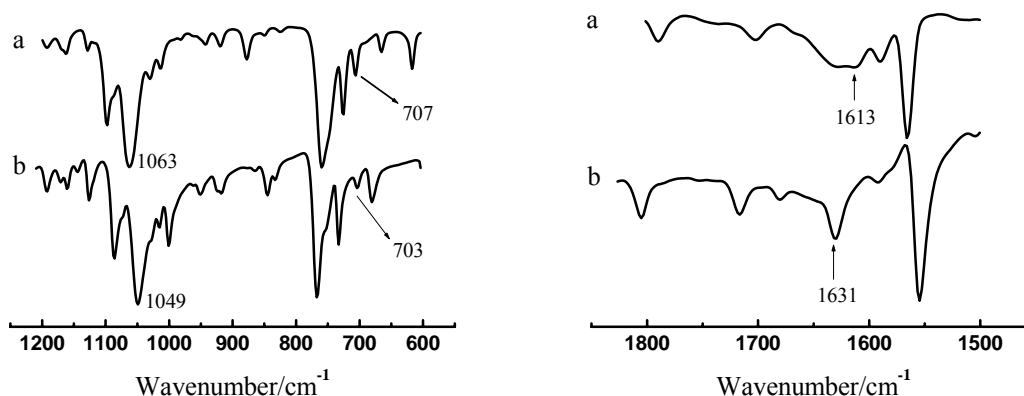
Table 1. Effect of Stripping Agents on the Recovery of Palladium(II)

Stripping Agents	% Recovery				
	0.5 M	1 M	2 M	3 M	5 M
HCl	0.00	0.00	0.00	0.00	0.00
HNO ₃	0.00	0.00	0.00	0.00	0.00
NaOH	35.8	32.5	31.4	30.7	27.3
NH ₃ ·H ₂ O	97.6	99.2	99.5	99.6	99.6
Na ₂ SO ₃	12.4	10.6	9.8	7.5	4.4

Figure 4. Plot of Log D versus Log [ABS O]. [Pd(II)] = 100 mg·L⁻¹; ■: 0.1 M HCl; ▲: 1.0 M HCl.**Figure 5.** Plot of Log D versus Log [Cl⁻]. [Pd(II)] = 100 mg·L⁻¹; HCl = 0.1 M; Organic phase: 0.5 M ABS O in benzene.

IR spectra of extracted Pd(II)-ABS O adduct

Extracted Pd(II)-ABS O adduct may be prepared by following procedure: 0.5 M ABS O in benzene was shaken with Pd(II) aqueous solution (1.0 g·L⁻¹ in 0.1 M HCl) many times until a saturated extraction organic phase was obtained. After removing benzene by distillation, a yellowish solid complex was obtained and dried in vacuum. Figure 6 shows the IR spectra of ABS O and Pd(II)-ABS O complex. The ν_{S-O} of free ABS O ligand appears as a strong absorption at 1049 cm⁻¹. In the extracted complex, the characteristic ν_{S-O} absorption appears at 1063 cm⁻¹ and it does not shift remarkably as compared to ν_{S-O} of a wide variety of metal-sulfoxide complexes [22-24]. This suggested that ABS O is not coordinated with palladium through the O or S atoms. In addition, the peak at 704 cm⁻¹ attributed to the absorption of ν_{C-S-C} of the benzothiazolyl ring [25] appears at 707 cm⁻¹ in the Pd(II)-ABS O complex, indicating that the S atom is not coordinated with the metal ion too. The C=N stretching vibration observed at 1631 cm⁻¹ for ABS O is shifted to 1613 cm⁻¹ in the Pd-ABS O complex, and the shift extent is similar to the Pd(II)-imidazole complex [26,27]. These facts indicated that ABS O is coordinated with Pd (II) via nitrogen atom on the thiazole ring, which is similar to the binding of benzothiazole derivatives to a number of other metals reported previously [28-32].

Figure 6. Infrared spectra of Pd(II)-ABS0 complex (a) and ABS0 (b)*X-Ray Crystallography of PdCl₂(ABS0)₂* [33]

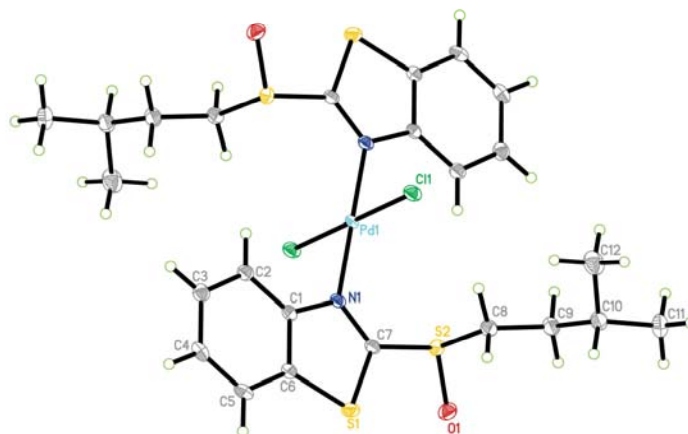
The crystal structure of PdCl₂(ABS0)₂ is shown in Figure 7. Crystallographic data and some experimental conditions used to obtain the intensity data are given in Table 2. As expected, in Pd(II)-ABS0 complex, ABS0 acts as neutral unidentate ligand coordinating to palladium via the thiazolyl N atom. The complex is of trans-conformation and Pd(II) is coordinated by two Cl atoms and two ABS0 at opposite position. Two opposite Pd-N and Pd-Cl bond distances are equivalent respectively. The Pd-atom and two N-atoms are coplanar (N(1)-Pd(1)-N(1)# = 180.00°). Thus, the palladium-ABS0 complex as a whole is in complete symmetry with palladium atom at the symmetry center of the square-planar complex. This is similar to bis[2-(2-benzoxazolyl)phenol-N]dichloropalladium(II) [34].

Table 2. Crystal data and structure refinement details

Empirical formula	C ₂₆ H ₃₂ Cl ₈ N ₂ O ₂ PdS ₄	Density (calculated)	1.658 g/mL
Formula weight	922.78	Absorption coefficient	1.334 mm ⁻¹
Temperature	100(2) K	F(000)	928
Wavelength	0.71073 Å	Crystal size	0.25 x 0.08 x 0.08 mm ³
Crystal system	Monoclinic	θ range for data collection	2.53 to 28.29°
Space group	P2(1)/c	Reflections collected	13380
Unit cell dimensions	a = 18.0079(15) Å, α = 90° b = 6.0692(5) Å, β = 116.5450(10)° c = 18.9080(16) Å, γ = 90°	Independent reflections	4358 [R(int) = 0.0367]
Volume	1848.7(3) Å ³	Final R indices	R1 = 0.0364, wR2 = 0.0811
Z	2	[I > 2σ(I)]	
		Goodness-of-fit on F ²	1.051
		R indices (all data)	R1 = 0.0494, wR2 = 0.0862
		Largest diff. peak and hole	1.350 and -0.811 e.Å ⁻³

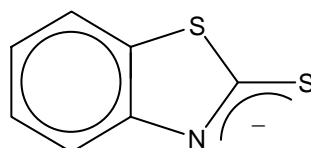
The Pd-N and Pd-Cl distances are 2.015(2) and 2.2919(6) Å. These values are a little shorter than the values expected from the sum of Shannon's ionic radii [35] (Pd-N = 2.10; Pd-Cl = 2.45 Å). The Pd-N bond length is longer than the values reported for bis[2-(2-benzoxazolyl)phenol-*N*]dichloro palladium (Pd-N 2.002 Å) [34]. Bond angles around the central Pd atom show small deviations from the idealized value of 90° (N(1)-Pd(1)-Cl(1) = 90.69°, N(1)-Pd(1)-Cl(1)# = 89.31°).

Figure 7. Molecular structure of PdCl₂(ABSO)₂ and the atomic labeling



Almost all C-C-C bond angles of ABSO phenyl ring are about 120°, except that the angles of C(1)-C(2)-C(3), C(4)-C(5)-C(6) are a little smaller (117.9° and 117.1°). The bond lengths and angles in the thiazole unit are essentially similar to those reported for thiazole units in [Rh{bis(benzothiazol-2-yl)ethane}(CO)₂]BF₄ [29], [ReOCl₃(2-(2-pyridyl)benzthiazole)] [31], [cis-dichloro(2-pyrid-2-ylbenzothiazole)platinum(II)] [32]. The N(1)-C(7) bond length (1.306(3) Å) are between the single and double bond (according to Pauling's presentation, the bond lengths of C-N and C=N are 1.47 and 1.29 Å respectively [36]), which may result from the fact that the benzothiazole-2-thiolate group has the following resonance structure (Figure 8) [37], namely, the negative charge of S(2) is partially delocalized to the N atom. S-O bond length (1.487(2) Å) is consistent with a considerable double bond character and similar to the lengths of uncoordinated sulfoxides [38].

Figure 8. Resonance structure of benzothiazole-2-thiolate group



Conclusions

A new sulfoxide extractant, iso-amyl benzothiazolyl sulfoxide (ABS_O) was synthesized and used in the solvent extraction of Pd (II) from hydrochloric acid media. The extraction of Pd (II) was quantitative from 0.1 M HCl with 0.5 M ABS_O in benzene. The pH of aqueous solution did not affect the extraction process of Pd (II) when $[H^+] \leq 2$ M. IR and X-ray crystal structure analysis of Pd(II)-ABS_O extraction adduct indicated that ABS_O acts as neutral unidentate ligand coordinated with palladium via the thiazole N atom, which is quite different from general alkyl sulfoxides which is coordinated with Pd (II) via O or S atoms of the ligands.

Acknowledgements

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Experimental

General

The concentration of palladium in the aqueous phase was determined with a Shimadzu Model AA-680 atomic absorption spectrophotometer. IR spectra were obtained for KBr pellets using a VECTOR33 IR spectrophotometer (Bruker). ¹H-NMR spectra were performed on an AVANCE Digital 400 MHz NMR Apparatus (Bruker). FAB-MS spectra were obtained with Finigan-2000 mass apparatus.

Preparation of iso-amyl benzothiazolyl sulfide (2)

2-Mercaptobenzothiazole (250.9 g, 1.5 mol), acetone (500 mL), water (50 mL) and KOH (120 g, 2.1 mol) were put in a round-bottom flask fitted with a mechanical stirrer and condenser and the mixture was heated for about 30 min. Iso-amyl bromide (302.1 g, 2.0 mol) was then added gradually with stirring through a dropping funnel and the reaction mixture was refluxed for 5 hours. The residual solid was filtered after cooling down and the acetone was removed by distillation. The organic phase was diluted with ether (50 mL), washed with water three times and dried with anhydrous Na₂SO₄. The ether was evaporated and 281.3 g (yield: 79%) of a brown liquid product was obtained. FT-IR (KBr): 3062.7 (=CH), 2994.80, 2958.66, 2931.01, 2871.73 (-CH₂-, -CH₃), 1559.57, 1459.58 (C=C), 1427.75, 1365.58 (-C(CH₃)₂), 1237.42, 1183.39 (C-S-C), 886.77 (C-N), 757.48, 727.05 cm⁻¹.

Iso-amyl benzothiazolyl sulfoxide (ABS_O, 3):

Iso-amyl benzothiazolyl sulfide ether (2, 142.4 g, 0.6 mol) was placed in a round-bottomed flask fitted with a mechanical stirrer and condenser and a mixture of acetic acid (100 mL) and acetone (100 mL) were added. H₂O₂ (30%, 150 mL) was added gradually through a dropping funnel and the reaction

mixture was stirred for 2 hour at room temperature, then it was poured into ice-water, the organic phase was collected and the acetone was further removed by distillation. The yellow crude product was crystallized from ethanol and 125.4 g of colorless crystals were obtained (yield: 82.5%). FT-IR (KBr): 3061 (=CH), 2952, 2924, 2913, 2869 (-CH₂-, -CH₃), 1631 (-C=N-), 1555, 1471, 1455 (C=C), 1425, 1385 (-C(CH₃)₂), 1049 (S=O), 845 (C-N), 767, 733cm⁻¹; ¹H-NMR (CDCl₃): δ (ppm) 8.04-8.02 (1H, =CH), 7.97-7.95 (1H), 7.54-7.50 (1H), 7.47-7.43 (1H), 3.27-3.09 (2H, CH₂-C), 1.86-1.65 (2H, C-CH₂-C), 1.58-1.52 (1H, -CH-), 0.91-0.88 (6H, 2CH₃); FAB-MS (M+1)/z: 254.1.

Pd (II) stock solution (1.0 g·L⁻¹):

A weighed portion of palladium metal was dissolved in aqua regia (40 mL). When the metal was completely dissolved, the solution was evaporated to approximately 5 mL. Residual HNO₃ was removed by adding concentrated HCl (12 M, 50 mL) and evaporating to approximately 5 mL again, and this was repeated 3 times. Then the solution was evaporated to dryness. The solid was dissolved and diluted to 1000 mL with 0.1 M HCl. Working solutions were prepared by further dilution and standardized HCl solutions were added to adjust the H⁺ concentration to the desired value. All the chemicals used were of analytical reagent grade. Double-distilled water was used throughout.

General extraction procedure

Experiments were carried out by shaking equal volumes (10 mL) of the aqueous and organic phases in stoppered glass tubes. The aqueous phase containing 100 mg·L⁻¹ palladium(II) was equilibrated for 15 min with 0.5 M ABSO in benzene. The two phases were then allowed to settle and separate and an aliquot was taken from the aqueous phase for analysis of the metal concentration by atomic absorption spectrophotometer at 247.6 nm. The metal concentration in the organic phase was determined by mass balance of the metal before and after extraction. All experiments were performed at a controlled temperature of 22±1°C.

X-ray crystal structure determination

The crystal of extracted Pd(II)-ABSO complex was grown by slow evaporation of CH₃Cl and hexane mixed solutions at room temperature. A single crystal with approximate dimensions of 0.25 x 0.08 x 0.08 mm³ was selected and sealed in a thin-walled glass capillary for structural analysis. Diffraction data were collected at 100K on a Bruker Apex CCD Area Detector, by using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). Semi-empirical absorption correction was applied. The structure was solved by using Bruker SHELXTL (Version 6.10) program package. All non-hydrogen atoms were refined anisotropically, hydrogen atoms were introduced at calculated positions and refined via a riding model.

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33. CCDC 262327 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk)
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Sample availability: Samples are available from the corresponding author.

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