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Thermal, fluorescence, structural and solution studies of a thallium(I) one-dimensional coordination polymer with 4-aminobenzoate (AB−), [Tl(μ4-AB)]n

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Abstract

A thallium(I) one-dimensional polymer, [Tl(μ4-AB)]n (1) [HAB = 4-aminobenzoic acid], has been synthesized and characterized. The single-crystal X-ray data of compound show the coordination number in the Tl^I ions is five, the thallium atoms have irregular coordination sphere containing stereo-chemically active lone pair and bi-hapto (η^2) interactions, thus attaining a total hapticity of seven with environment C_2O_5Tl. The thermal stability of 1 was studied by thermal gravimetric (TG) and differential thermal analyses (DTA). The ligand HAB and compound 1 are luminescent in the solution state, with emission maxima at 395 nm. The results of studies of the stoichiometry and formation of complex of 1 in DMF solution were found to be in support of their solid state stoichiometry.
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Keywords: Thallium(I); 4-Aminobenzoic acid; Coordination polymer; Lone pair

1. Introduction

Metal–organic coordination polymers are attracting a great deal of attention because of their potential as functional materials [1]. In metal–organic crystal engineering, one takes advantage of the coordinating ability of metal centers and organic ligands in order to build new coordination polymers. The main goal in metal–organic crystal engineering is to predict the topology of supramolecular architectures in order to synthesize extended solid-state materials with desired properties. However, there still remain many problems to overcome before the synthesis of coordination polymers with a desired topology is possible. Many parameters are involved in the formation of the metal–organic framework (MOF), such as the metal and its possibilities of coordination, the nature of the counter-anion, the metal-to-ligand ratio, the flexibility of the organic building blocks, the number and orientation of the coordinating sites in the organic spacers, and the solvent of recrystallization, among others [2]. The Tl^I compounds are interesting and frequently discussed in considering the "stereo-chemical activity" of valence shell electron lone pairs, potential ability to form metal–metal bonds and also complexes with aromatic hydrocarbons [3–8]. From recent structural study of Tl(I) complexes of anthranilates and salicylates [5], it has been argued that polyhapto-aromatic interactions also play an important role in determining the solid state lattices of such compounds. The "inert-pair effect" has, in a general way, been explained by Pitzer [9] and by Pyykkö and Desclaux [10] causing the outer s electrons to be more strongly attracted to the nucleus than normally expected. A theoretical study of relativistic effects and electron correlation effects in group 13 and period 6 hydrides and halides by Peter Schwerdtfeger et al. [11] shows that although relativistic contributions play an important role in the chemistry of the 6th period elements, there is no evidence that the 6s electrons are more inert than the s electrons of lighter elements. Thus, there is no special "inert-pair effect" for

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the 6th period elements, and it is inappropriate to use this term to designate the low valancies of heavier elements, in addition it is true that, in many of the reported Tl^I compounds [11] the s electrons play only a small part in bonding and in that sense can be regarded as core like, even for the lighter elements. Thus, σ-bonding involves mainly the valence p electrons, and the familiar concept of s–p hybridization has to be taken with care [11].

In several organometallic compounds, the stereoactive lone pair is manifested by a ''half-naked'' cation, with ligands only coordinating one hemisphere, as observed in the crystal structure of $[Tl_2(\mu\text{-Htdp})_2(\mu\text{-H}_2O)]_n$ (H_2tdp = 4,4-thiodiphenol) [12], where the lone pair occupies the hemisphere of Tl(I) coordination sphere with an obvious gap in the coordination sphere due to the lone pair. Our search show that Zn(II), Co(II), Cd(II) [13] and Ag(I) [14] coordination polymers of 4-aminobenzoic acid (HAB) were recently reported and similar coordination polymers of thallium(I) ion with benzoate-derived ligands were reported in the works by Schmidbaur and Wiesbrock [5,6] and by Kristianson [8]. Continuing with our previous work on Tl^I coordination polymers [12,15–22], in this work we wish to report a coordination polymer of Tl(I) with HAB via hydrogen bonds and covalent bonds with thermal, emission and solution studies of this compound.

HAB
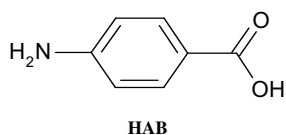
2. Experimental

2.1. Materials and physical techniques

All chemicals were of reagent grade and were used as commercially obtained without further purification. IR spectra were recorded using Perkin–Elmer 597 and Nicolet 510P spectrophotometers. Microanalyses were carried out using a Heraeus CHN–O-Rapid analyzer. Melting points were measured on an Electrothermal 9100 apparatus and are uncorrected. The thermal behavior was measured with a PL-STA 1500 apparatus. The luminescent properties were investigated with a Shimadzu RF-5000 spectrofluorophotometer. All UV–Visible spectra were recorded on a computerized double-beam Shimadzu 2550 spectrophotometer, using two matched 10-mm quartz cells. Conductometric measurements were carried out with a Metrohm 712 conductometer equipped with a Julabo F12-MB circulator. Crystallographic measurements were made at 298(2) K using a Bruker SMART APEX2 CCD area detector. The intensity data were collected using graphite monochromated Mo–Kα radiation ($\lambda = 0.71073$ Å). Accurate unit cell parameters and the orientation matrix were obtained from least–squares refinement. The structure has been solved by

Table 1
Crystal data and structure refinement for compound $[Tl(\mu_4\text{-AB})]_n$ (**1**)

Identification code	**1**
Empirical formula	$C_7H_6NO_2Tl$
Formula weight	340.50
Temperature	298(2)
Wavelength	0.71073
Crystal system	Cubic
Space group	$Iba2$
Unit cell dimensions	
a (Å)	14.652(3)
b (Å)	15.095(3)
c (Å)	6.9642(14)
α (°)	90.00
β (°)	90.00
γ (°)	90.00
Volume (Å^3)	1540.3(5)
Z	8
D_{calc} (g cm^{-3})	2.937
Absorption coefficient (mm^{-1})	20.12
$F(000)$	1216
Crystal size (mm^3)	$0.28 \times 0.21 \times 0.13$
Theta range for data collection (°)	1.94–25.28
Index ranges	$-17 \leqslant h \leqslant 17$
	$-18 \leqslant k \leqslant 18$
	$-8 \leqslant l \leqslant 6$
Reflections collected	1179
Independent reflections	1083
Absorption correction	Multi-scan
Maximum and minimum transmission	0.065 and 0.006
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	1179/1/89
Goodness-of-fit on F^2	1.055
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0320$
	$wR_2 = 0.0684$
R Indices (all data)	$R_1 = 0.0287$
	$wR_2 = 0.0671$
Largest difference Peak, hole	1.552 and -0.980 e Å^{-3}

direct methods and refined by full-matrix least-squares techniques on F^2 using SHELXTL [23]. The molecular structure plots were prepared using ORTEP and Mercury [24]. Crystallographic data and details of the data collection and structure refinements are listed in Table 1. The observed anisotropic thermal parameters, the calculated structure factors, and full lists of bond distances, bond angles and torsion angles are given in the Supplementary material.

3. Synthesis of $[Tl(\mu_4\text{-AB})]_n$ (**1**)

4-Aminobenzoic acid (1 mmol, 0.137 g) was dissolved in 20 ml methanol and was mixed and stirred with solution of 1 mmol (0.057 g) KOH in 3 ml H_2O, then a solution of 1 mmol (0.266 g) $TlNO_3$ in 5 ml H_2O was added to the mixture and was refluxed for 3 h. After filtering it was allowed to evaporate for several days and then suitable white crystals were obtained. The crystals were washed with acetone and air dried, s.p. = 222 °C, Yield: 0.163 g (48%). IR (selected bands; in cm^{-1}) : 490 m, 610 s, 777 s, 846 m, 1074 m, 1123 m, 1167 s, 1260 s, 1285 s, 1359 vs, 1395 vs, 1482 vs, 1540 vs, 1588 vs, 3195 m and 3395 m. Anal. calc.

for $C_7H_6NO_2Tl$: C, 24.67; H, 1.76; N, 4.11. Found: C, 24.80; H, 1.57; N, 4.60%.

4. Results and discussion

4.1. Structure description

The reaction between 4-aminobenzoic acid and $Tl^I(NO_3)$ provided crystalline materials of the general formula $[Tl(\mu_4-AB)]_n$ (1). Determination of the structure of the compound **1** by X-ray crystallography (Tables 1 and 2) showed the complex to be a novel one-dimensional polymer. There are five (TlO_5) coordinate Tl atoms (Fig. 1) and each AB^- anion has five bonding interactions and four lone pairs of AB^- connect to four Tl^I ions (Fig. 2). The carboxylate group of each AB^- ligand acts as both bidentate chelating, and bridging group where two oxygen atoms of the carboxylate group coordinate to a thallium(I) ion, also one of this oxygen atoms bridges to one other thallium

atoms and another oxygen atom bridges to two other thallium atoms. The amine nitrogen atom does not link to any thallium atom. The oxygen atom of carboxylate groups and hydrogen atom of $-NH_2$ groups of 4-aminobenzoate (AB^-) anions in compound **1** are involved in a hydrogen bonding network (Fig. 3).

In compound **1**, the lone pair of Tl(I) is 'active' in the solid state [5]. However, the arrangement of O-atoms suggest a gap or hole in coordination geometry around the Tl(I) coordination sphere (Figs. 1 and 2), a gap possibly occupied by a 'stereo-active' electron lone pair. Hence, the geometry of the nearest coordination environment of every Tl(I)-atoms is likely to be caused by the geometrical constraints of coordinated O-atoms, and by the influence of a stereo-chemically 'active' electron lone pair.

With low coordination number of 5 for large thallium(I) ions in compound **1**, one tends to look for secondary interactions that could possibly relieve this coordinative unsaturation. To find secondary interactions and any other
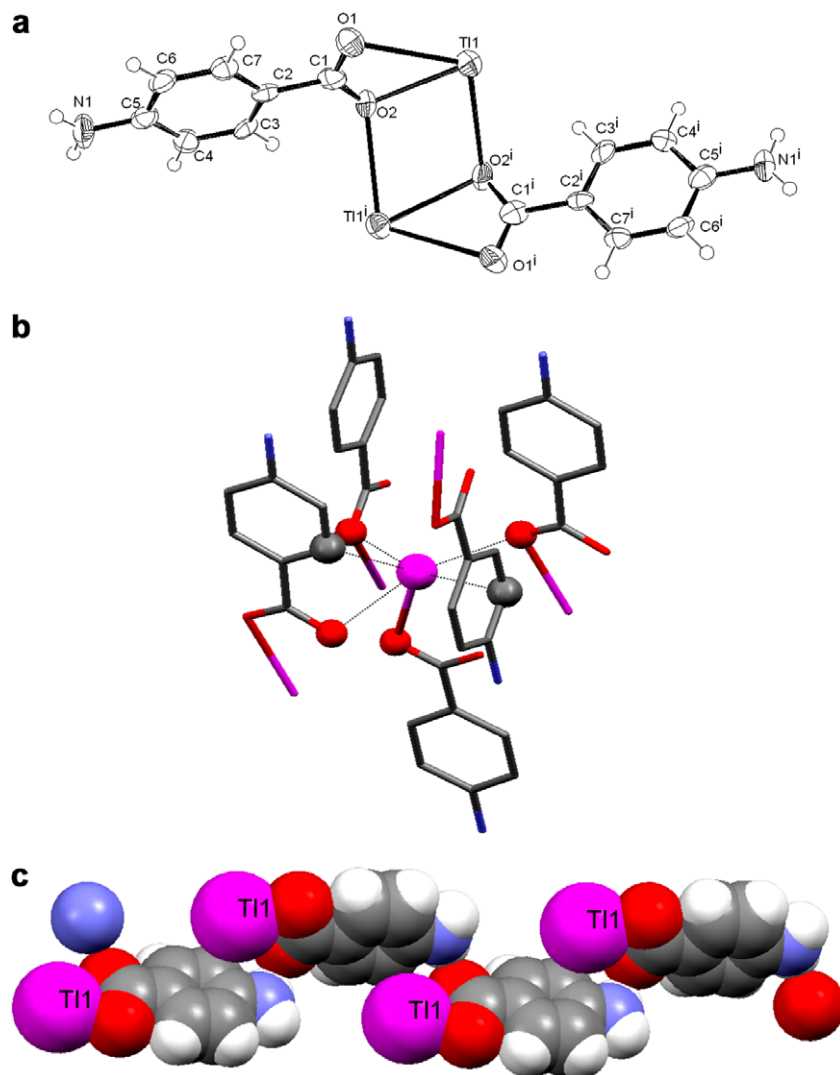

Fig. 1. (a) ORTEP diagram of compound **1**. (b) Environment of Tl-atoms in compound **1** after extending the bonding limit, Tl · · · C interactions. (c) Space-filling representation, close approaches of Tl to the face of phenyl rings can be seen (Tl = purple, O = red, C = gray, H = white). (i) $-x$, $-y$, z. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
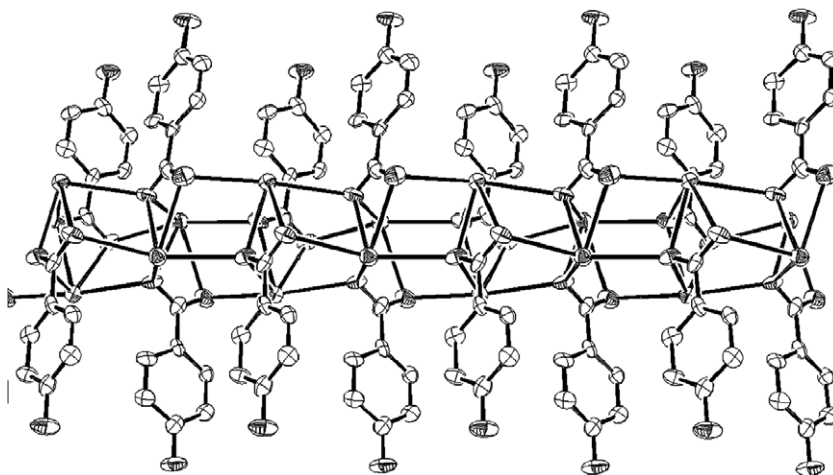
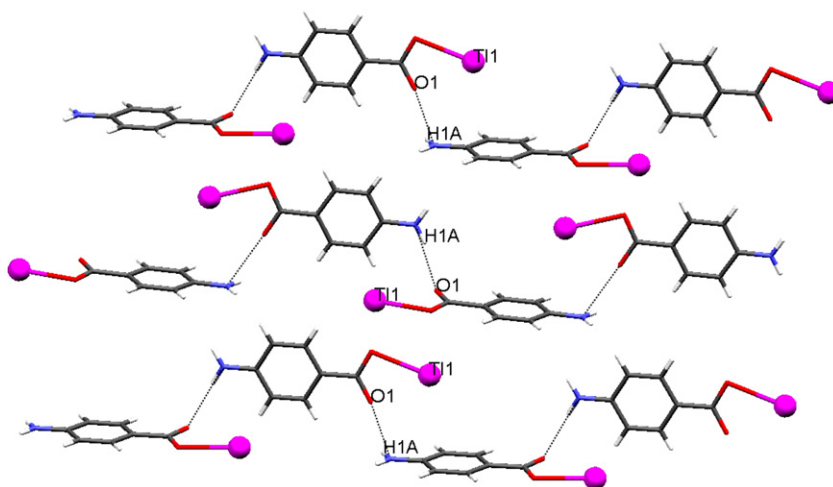Fig. 2. A fragment of the one-dimensional polymer in compound **1**. H atoms are omitted for clarity.

Fig. 3. Showing hydrogen bonding in the compound **1**.

potential donor center the bonding limit to be extend and a search was made for Tl⋯C approaches. Our search show that Tl in compound **1** may also be involved in an η^2 interactions with the phenyl groups of neighboring molecules (Fig. 1b and c). Thus, the Tl(I) atoms are linked to two carbon atoms of phenyl groups with distances Tl⋯C of 3.362(2) and 3.617(5) Å. Hence, the Tl(I) coordination sphere is completed and rather than a TlO₅ coordination sphere, the complex can be considered to contain an η^2 (C₂O₅Tl) center with a seven coordination number. The reported Tl⋯C separations range is 3.20–4.00 Å in recent reported species [5,25] and the sum of the vander Waals radii of carbon and Tl atoms is 3.66 Å [26]. Thus, η^2 aromatic coordination of Tl(I) appears to be yet another

factor which can make varying contributions to the stability of complex.

5. Thermogravimetric analysis

To examine the thermal stability of compound **1**, thermal gravimetric (TG) and differential thermal analyses (DTA) were carried out between 30 and 700 °C in the static atmosphere of air (Fig. 4). Compound **1** does not melt and TG curve exhibits a very sharp loss of weight between 222 and 239 °C with a mass loss of 92.3% that could be related to sublimation of this compound. DTA curve displays only a broad exothermic peak with a maximum intensity at 322 °C.

6. Luminescent properties

The UV–Vis and emission spectra of complex **1** as well as the pure ligand HAB were studied. The UV–Vis spectra of both ligand and complex in DMF display intense

Table 2
Selected bond lengths (Å) and angles (°) for compound [Tl(μ₄-AB)]ₙ (**1**)

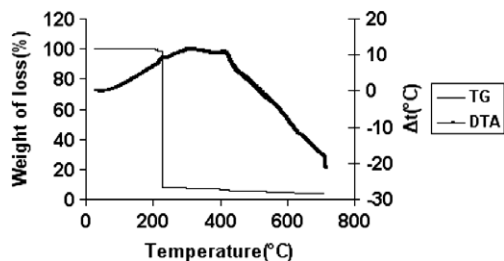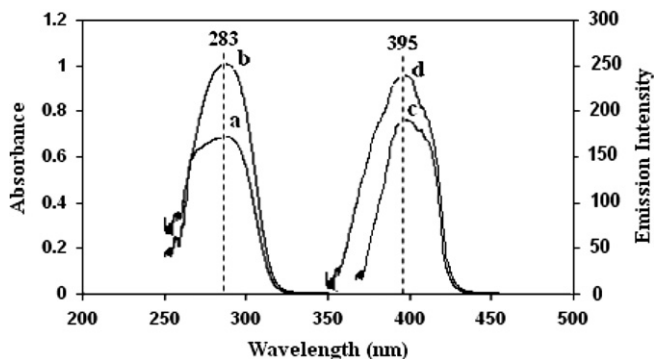| Tl1–O2	2.633(7)	O2–Tl1–O2	70.2(3)
Tl1–O2^i	2.772(8)	O2–Tl1–O1	48.4(2)
Tl1–O1	2.786(8)	O2–Tl1–O1	112.1(2)

(i) −x, −y, z.

Fig. 4. Thermal behaviour of compound **1**.

Fig. 5. Electronic absorption of ligand HAB (a), Electronic absorption of compound **1** (b) Absorption: $c = 5.0 \times 10^{-5}$ mol l^{-1}, DMF, $d = 1$ cm for both ligand HAB and compound **1**. Solution-state emission spectrum for compound **1** (c). Solution-state emission spectrum for ligand HAB (d). Room temperature, $\lambda_{exc} = 350$ nm.
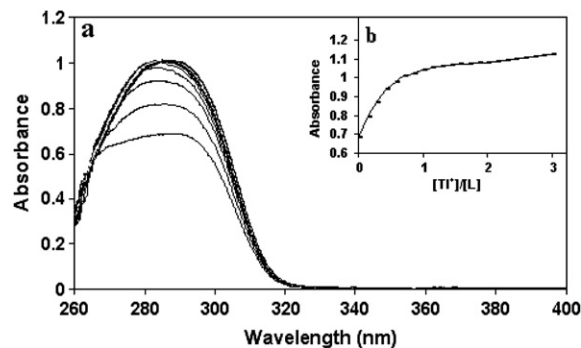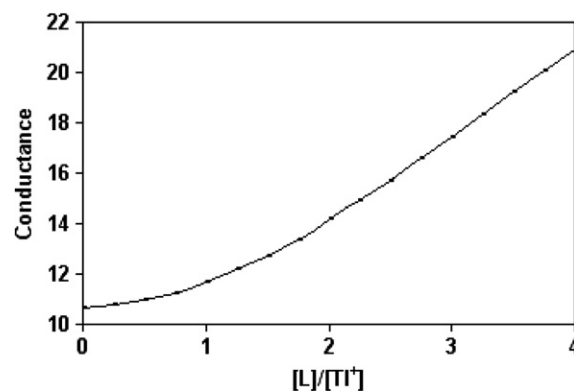

Fig. 6. (a) Electronic absorption spectra of ligand HAB in DMF (5.0×10^{-5} M) in the presence of increasing concentration of thallium(I) ion at room temperature and (b) corresponding mole ratio plot at 283 nm.

Fig. 7. Conductivity vs. [L]/[Tl$^+$] mole ratio plot DMF solution.

absorption bands with the maximum intensity at 283 nm (Fig. 5a and b, respectively), indicating that electronic transitions are mostly of π–π^* character, originating from the aromatic groups of the ligand. In DMF emission bands have been observed both for compound **1** and also the ligand HAB at 395 nm upon excitation at 350 nm, (Fig. 5c and d, respectively). The emission intensity of compound **1** is fairly weaker than that of the uncoordinated ligand, which can be attributed to the heavy atom effect [27,28] due to the coordination of the ligand to the Tl(I) center. Thus, compounds **1** may have potential applications as a luminescent material in organic light emitting devices.

7. Solution studies

The electronic absorption spectra of the ligand AB$^-$ in the presence of increasing concentration of thallium(I) ion in DMF at room temperature are shown in Fig. 7. As is obvious, the strong absorption of ligand at 283 nm increases with increasing concentration of the metal ion. The resulting absorbance (at 283 nm) against [Tl$^+$]/[L] mole ratio plot, shown in the inset of Fig. 6, revealed a distinct inflection point a metal-to-ligand molar ratio of about 1, emphasizing the formation of a 1:1 complex in solution. The formation and stoichiometry of the Tl$^+$–L complex in DMF solution was also investigated by a conductometric method. The conductivity of a 5.0×10^{-5} M solution of

thallium(I) nitrate solution in DMF was monitored as a function of [L]/[Tl$^+$] mole ratio at 25.00 ± 0.05 °C and the resulting plot is shown in Fig. 7. As it is seen, the initial conductivity is relatively low, probably due to some degree of ion pairing which is common in solvents of relatively low dielectric constant like DMF. Addition of the ligand to the metal salt solution then do not causes a variation in the solution conductivity possessing a rather distinct inflection point at a molar ratio of about one, indicating the formation of a 1:1 Tl$^+$–L complex in solution.

For evaluation of the conditional formation constants, the mole ratio data obtained by the two different physico-chemical methods employed were fitted to the previously reported equations [29,30] using a non-linear least-squares curve fitting program KINFIT [31]. The conditional formation constants of the complex were evaluated as 0.60 ± 0.02 and 0.52 ± 0.03 from the spectrophotometric and conductometric methods, respectively.

8. Conclusions

A Tl^I one-dimensional coordination polymer of 4-aminobenzoic acid (HAB) ligand, [Tl(μ_4-AB)]$_n$, was synthesized and characterized. The aromatic carboxylate ligand in this complex exhibits a less-common η^2-coordination mode of the phenyl rings, in addition to the normal carboxylate

coordination modes. The individual one-dimensional units in the compound $[Tl(\mu_4\text{-}AB)]_n$ are almost parallel to each other and further linked by hydrogen bonding, resulting in a two-dimensional framework. The results of studies of the stoichiometry and formation of $[Tl(\mu_4\text{-}AB)]_n$ in DMF solution were found to be in support of their solid state stoichiometry. This compound has shown luminescent properties in DMF solution.

Acknowledgement

Appendix A. Supplementary material

CCDC 645563 contains the supplementary crystallographic data for **1**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2007.07.043.

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