  Bull. Chem. Soc. Jpn., 60, 3207—3211 (1987)

Synthesis, and Crystal and Molecular Structure of Bis[2-(2-benzoxazolyl)-phenolato]nitratoiron(III), $Fe(C_{13}H_8O_2N)_2(NO_3)$

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(Received March 17, 1987)

The title complex was newly synthesized and its crystal and molecular structure was determined by the single-crystal X-ray diffraction technique. The crystal is monoclinic, space group $C2/c$, a=16.005(4), b=10.520(2), c=15.338(4) Å, β=114.68(2)°, and Z=4. In the complex, the central metal atom is hexa-coordinated being in a deformed octahedral geometry: Two 2-(2-benzoxazolyl)phenolato ligands form six-membered chelate rings being coordinated with their oxazolyl nitrogen and phenolato oxygen atoms, while the nitrate ion acts as a bidentate with its two oxygen atoms. As the benzoxazolyl ring is parallel and overlapped with that of the neighboring complex along the c-axis, where the interplane distance is 3.557 Å, some interaction between the rings is expected. As this complex in solid state is deep violet, almost black, in color, some charge-transfer bands are expected to exist in its electronic spectra. The bis[2-(2-benzothiazolyl)phenolato]-nitratoiron(III) was found to be isomorphous to the title complex.

The 2-(2-benzoxazolyl)phenol (Hbxp) is known as a chelating reagent for many bivalent metals. Analyses of zinc(II), cadmium(II), palladium(II), and copper(II) using Hbxp as the colorimetric reagent, have been reported in several literatures.[1-4] The crystal structures of copper(II) and cadmium(II) salts of Hbxp ($M(bxp)_2$, M=Cu, Cd) were already determined by the single-crystal X-ray diffraction method.[5] The 2-(2-benzothiazolyl)phenol (Hbtp) is also a good analytical reagent which forms stable complexes with bivalent metals. An analytical chemistry study of its metal complexes had been presented by Charles and Freiser[6] and the authors have investigated the solvent-extraction of some metals using Hbtp.[7]

However, there have been yet very few studies about the tervalent metal complexes of bxp and btp, nor any reports of their structure.

This time, we could obtain the iron(III) salts of both Hbxp and Hbtp, $Fe(bxp)_2(NO_3)$ (**1**) and $Fe(btp)_2(NO_3)$ (**2**), though the FeL_3 type complex was not obtained. Both salts resemble each other in color (deep violet, almost black), in their solubilities in various solvents, as well as in their crystal forms. As **1** and **2** were found to be isomorphous, the crystal and molecular structure of **1** was determined by the single-crystal X-ray diffraction technique.

Experimental

Synthesis of Bis[2-(2-benzoxazolyl)phenolato]nitratoiron-(III) (1). The solutions of iron(III) nitrate enneahydrate (0.81 g, 2.0 mmol in 30 cm³ of ethanol), and of Hbxp (1.69 g, 8 mmol in 200 cm³ of ethanol) were mixed and stirred. After left standing the mixed solution overnight, the precipitate was filtered off, washed with a small portion of ethanol, and dried in vacuo over silica gel. Yield, 0.54 g (50%). Found; Fe, 10.44; C, 58.09; H, 2.99; N, 7.78%. Calcd for ($FeC_{26}H_{16}O_7N_3$); Fe, 10.38; C, 58.02; H, 3.00; N, 7.81%.

Synthesis of Bis[2-(2-benzothiazolyl)phenolato]nitratoiron-(III) (2). The solutions of iron(III) nitrate enneahydrate (0.81 g, 2.0 mmol in 30 cm³ of ethanol), and of Hbtp (1.82 g, 8 mmol in 300 cm³ of hot ethanol) were mixed and stirred. The product began to precipitate soon, and the reaction was completed in several hours. The product was filtered off, washed with ethanol, and dried in vacuo over silica gel. Yield, 0.65 g (57%). Found; Fe, 9.63; C, 54.75; H, 2.87; N, 7.40; S, 11.22%. Calcd for ($FeC_{26}H_{16}O_5N_3S_2$); Fe, 9.79; C, 54.75; H, 2.83; N, 7.37; S, 11.24%.

The recrystallization of the products have been unsuccessful so far. From the solution of the complex in the solvents such as chloroform, ethanol, and others, only decomposition products were obtained when a part of the solvent was evaporated off.

Single-Crystal X-Ray Analysis. A crystal of **1** used for the X-ray analysis was chosen from the synthesized product. The crystallographic data and some experimental conditions used to obtain the intensity data are tabulated in Table 1. The reflections were collected on a Rigaku AFC-6A automated four-circle X-ray diffractometer with graphite monochromated Mo $K\alpha$ radiation (λ=0.71073 Å) (scan speed: 4° min⁻¹(θ)) using the ω—2θ scan technique.

Structure Determination. The structure of the complex

Table 1. Crystallographic Data and Some Experimental Conditions

Chemical Formula:	$FeC_{26}H_{16}O_7N_3$	F. W. 538.28	
Monoclinic		Space group:	$C2/c$
a(l/Å)	16.005(4)	(ϕ/°)	114.68(2)
b(l/Å)	10.520(2)	U(v/Å³)	2346.6(11)
c(l/Å)	15.338(4)	Z	4
D_m(d/Mg m⁻³)	1.50(3)	D_x(d/Mg m⁻³)	1.52
μ(Mo $K\alpha$)(n/mm⁻¹)	0.718	Final R value	0.070
Reflections measured		2208	
Reflections used for calculation[a]		1038	
Used crystal (v/mm³)		0.22×0.27×0.15	
Scan width (θ/°)		1.04+0.5 tan θ	
Scanned range (2θ/°)		3—50	

a) Reflections with $|F_o|>3\sigma(|F_o|)$ were used.

was solved by the heavy-atom method. The positions of the iron and some nitrogen and oxygen atoms were deduced from a three dimensional Patterson map, and the other non-hydrogen atoms were successively located by the repeated Fourier syntheses. Their positional, isotropic and then anisotropic thermal parameters were refined by a block-diagonal least-squares method. At the final cycle of the refinement with anisotropic temperature factors for all non-hydrogen atoms, all the parameter shifts were less than one-third of the corresponding standard deviations.

All the calculations were carried out on a HITAC-680H at the Computer Center of the University of Tokyo, using a local version of the UNICS program.[8] The atomic scattering factors were taken from Ref. 9.

Other Measurements. The X-ray powder patterns of the complexes were obtained by a diffractometer of Model DX-GO-F JEOL, using Cu $K\alpha$ radiation in the range of 4° to 35° in 2θ. Infrared spectra were measured with a JASCO IRA-1 type infrared spectrophotometer using KBr disk technique. The electronic spectra in chloroform solutions (immediately after dissolving the complexes) were obtained with a Shimadzu UV-240 spectrophotometer. Magnetic moments of the complexes were measured using a Gouy balance at ambient temperature.

Results and Discussion

The final atomic parameters and their equivalent thermal parameters of the complex are listed in Table 2, while the bond lengths and bond angles are tabulated in Table 3.[10] A perspective drawing of the complex around the metal atom including the overlapping benzoxazole ring of the neighboring complex are shown in Fig. 1, while the projection of a unit cell to the ac-plane in Fig. 2.

The central metal atom, as well as the N(N) and

Table 2. Final Atomic Coordinates ($\times 10^4$) with Estimated Standard Deviations in Parentheses, and Their Equivalent Isotropic Temperature Factors (B_{eq}/Å^2)

Atom	x	y	z	B_{eq}/Å^2 b)
Fe	5000	6450.8(19)	2500	4.2_8
N(N)	5000	8898(11)	2500	6.5_8
O(N1)	5000	10038(10)	2500	10.8_4
O(N2)	4323(4)	8231(6)	2465(4)	6.1_2
N(1)	5438(4)	6417(7)	3984(4)	4.0_7
O(1)	6416(4)	6277(5)	5515(3)	5.2_6
O(2)	6070(3)	5530(5)	2709(4)	5.0_7
C(1)	4958(5)	6686(8)	4545(5)	4.6_9
C(2)	5573(6)	6619(8)	5487(6)	5.3_0
C(3)	5350(7)	6805(8)	6270(6)	7.7_1
C(4)	4434(7)	7145(10)	6000(7)	8.5_0
C(5)	3778(7)	7193(9)	5033(7)	7.5_4
C(6)	4033(6)	6993(8)	4284(7)	6.5_0
C(7)	6286(5)	6182(7)	4589(5)	4.3_4
C(8)	7051(5)	5838(7)	4372(5)	3.9_4
C(9)	6919(5)	5542(8)	3441(5)	4.7_3
C(10)	7652(5)	5224(9)	3209(7)	6.0_1
C(11)	8535(6)	5218(9)	3968(7)	6.4_0
C(12)	8678(6)	5482(8)	4915(7)	6.0_5
C(13)	7936(5)	5803(8)	5144(6)	5.1_3

b) The equivalent isotropic temperature factors were computed using the following equation:
$B_{eq}=4/3(B_{11}a^2+B_{22}b^2+B_{33}c^2+B_{13}ac\cos\beta)$.
The B_{ij}'s are defined by:
$T=\exp[-(h^2B_{11}+k^2B_{22}+l^2B_{33}+2klB_{23}+2hlB_{13}+2hkB_{12})]$.

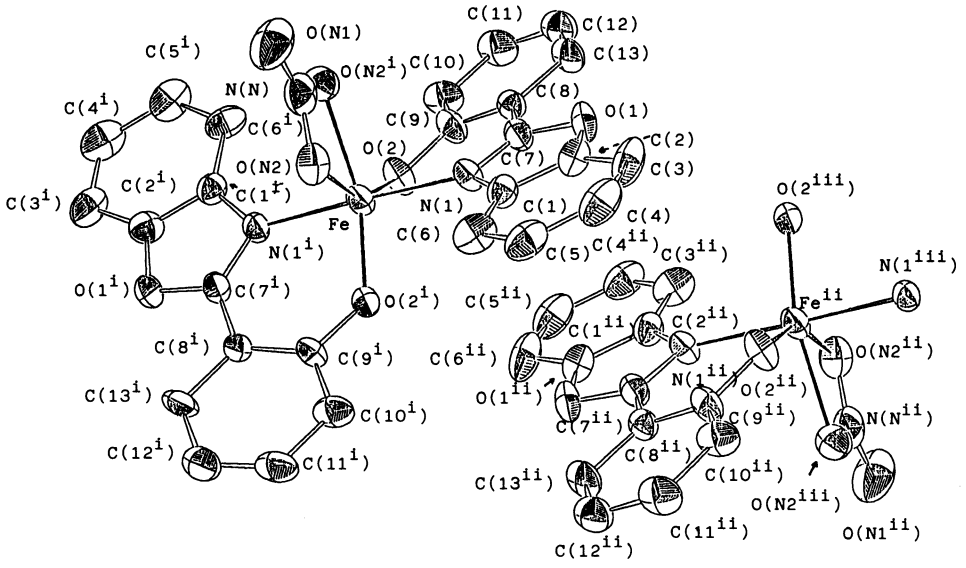

Fig. 1. A perspective drawing of a complex molecule together with the overlapping benzoxazole ring of the neighboring complex; the numbering scheme of the atoms is also shown.[11]

Table 3. Bond Lengths and Bond Angles of the Complex

Bond length	(l/Å)	Bond length	(l/Å)
Fe-O(N2)	2.154(7)	Fe-N(1)	2.084(12)
Fe-O(2)	1.875(6)	N(N)-O(N1)	1.199(15)
N(N)-O(N2)	1.273(11)	N(1)-C(1)	1.402(18)
O(2)-C(9)	1.354(10)	N(1)-C(7)	1.308(9)
O(1)-C(2)	1.379(13)	O(1)-C(7)	1.351(17)
C(1)-C(2)	1.369(16)	C(2)-C(3)	1.40(2)
C(3)-C(4)	1.392(16)	C(4)-C(5)	1.42(2)
C(5)-C(6)	1.39(2)	C(1)-C(6)	1.400(13)
C(7)-C(8)	1.441(16)	C(8)-C(9)	1.39(2)
C(9)-C(10)	1.401(18)	C(10)-C(11)	1.406(13)
C(11)-C(12)	1.40(2)	C(12)-C(13)	1.414(18)
C(13)-C(8)	1.417(11)		
Bond angle	**(ϕ/°)**	**Bond angle**	**(ϕ/°)**
N(1)-Fe-N(1^i)	178.1(5)	N(1)-Fe-O(N2)	88.8(4)
N(1)-Fe-O($N2^i$)	92.9(4)	N(1)-Fe-O(2)	86.4(4)
N(1)-Fe-O(2^i)	92.6(4)	O(N2)-Fe-O(2)	150.2(3)
O(N2)-Fe-O($N2^i$)	59.1(2)	O(N2)-Fe-O(2^i)	91.8(2)
O(2)-Fe-O(2^i)	117.8(3)	Fe-O(N2)-N(N)	93.9(5)
O(N2)-N(N)-O($N2^i$)	113.2(9)	O(N2)-N(N)-O(N1)	123.4(8)
Fe-N(1)-C(1)	130.3(7)	Fe-N(1)-C(7)	123.7(8)
N(1)-C(7)-O(1)	113.0(10)	C(2)-O(1)-C(7)	105.5(8)
O(1)-C(2)-C(1)	108.1(12)	N(1)-C(1)-C(2)	107.5(9)
N(1)-C(1)-C(6)	131.0(11)	O(1)-C(2)-C(3)	127.2(11)
N(1)-C(7)-C(8)	127.8(12)	C(6)-C(1)-C(2)	121.5(12)
C(1)-C(2)-C(3)	124.6(11)	C(2)-C(3)-C(4)	113.3(12)
C(3)-C(4)-C(5)	123.4(16)	C(4)-C(5)-C(6)	121.1(12)
C(5)-C(6-)C(1)	116.1(12)	O(1)-C(7)-C(8)	119.2(8)
C(7)-C(8)-C(9)	121.0(9)	C(7)-C(8)-C(13)	117.6(11)
C(13)-C(8)-C(9)	121.5(10)	C(8)-C(9)-C(10)	122.1(10)
C(9)-C(10)-C(11)	116.8(13)	C(10)-C(11)-C(12)	112.0(12)
C(11)-C(12)-C(13)	121.0(11)	C(12)-C(13)-C(8)	116.7(12)
Fe-O(2)-C(9)	131.7(7)	O(2)-C(9)-C(8)	121.6(10)
O(2)-C(9)-C(10)	116.4(12)		

Key to the symmetry operations: i, $1-x$, y, $0.5-z$.

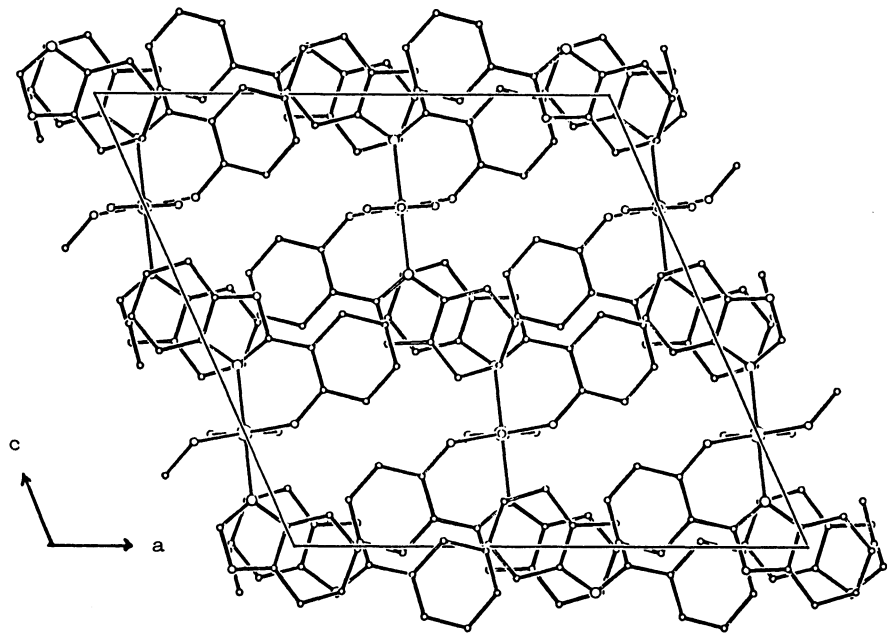

Fig. 2. A projection of the unit cell to the ac-plane.

O(N1) atoms of the nitrate ion are at the respective special positions: 0.5, y, 0.25. The metal atom is 2*N*4*O*-hexa-coordinated being in a deformed octahedral geometry. From both ends of an axis, two oxazole nitrogen atoms of the respective ligands, N(1) and N(1^{i})[11] are ligated. On the equatorial plane, two oxygen atoms of the phenolato groups of the ligands, O(2) and O(2^{i})[11], as well as two nitrato oxygen atoms of an ion O(N2) and O($N2^{i}$)[11] are coordinated to the metal atom. The oxazolyl oxygen atom, O(1), is not ligated to the metal atom. Thus the bxp anion forms a six-membered chelate ring, while the nitrate ion makes a four-membered ring.

The least-squares plane of O(2), O(2^{i}), O(N2), O($N2^{i}$), and Fe atoms[12] (average of the positional deviations of the atoms from the plane is 0.070 Å) is approximately perpendicular to Fe–N(1) (88.4°), and the angle N(1)–Fe–N(1^{i}) is 178.1(5)°. However, on the equatorial plane, the angles O(2)–Fe–O(2^{i}) and O(N2)–Fe–O($N2^{i}$) are 117.8(2), and 59.1(2)°, respectively: They deviate greatly from the right angle. The bond lengths Fe–N(1) and Fe–O(2) are 2.084(12) and 1.875 Å, respectively. As the sum of Shannon's ionic radii[13] are Fe–N, 2.11 and Fe–O, 2.00 Å, both of the observed values are shorter than the expected values. On the other hand, as Fe–O(N2) was found to be 2.154(7) Å, which is much longer than the sum of the ionic radii, the bond is thought to be weak. The two such weakly bonding oxygen atoms, O(N2) and O($N2^{i}$), are regarded as cooperating with each other and occupying one equatorial position of the trigonal-bipyramidal penta-coordination geometry.

The benzoxazole ring (A), the phenyl ring of the phenolato group (B), and the six-membered chelate ring (C) are about on the respective planes. The average deviations of the atoms from the respective ring planes are: (A) 0.011; (B) 0.011; and (C) 0.113 Å. The dihedral angles between the planes are: (A–B) 9.22; (A–C) 7.45; (B–C) 10.79°. As shown in Table 3, all the bond lengths of C–C, C–N, and C–O in the ligand bxp, including C(9)–O(2), are intermediate of the single and double bonding ones (according to Pauling's presentation; the single bonding and double bonding C–C, C–N, and C–O are: 1.544 and 1.334; 1.47 and 1.29; and 1.51 and 1.29° Å respectively[14]). Almost all C–C–C bond angles of the phenylene and phenyl rings of the ligand are about 120°. The angles of C(1)–C(6)–C(5) and C(2)–C(3)–C(4) are a little smaller, but these deviations were also found in those of the free ligand.[15] Consequently, the conjugated double bond system is likely extended all over the bxp ligand, probably including the chelate ring, too. The N(N)–O(N1) and N(N)–O(N2) lengths of the nitrate ion are 1.199(15) and 1.273(11) Å, respectively. Therefore, the N=O double bonding is a little localized in the former bond, although both of them are shorter than the single bonding N–O expected from the sum of the covalent bonding radii.[14]

As shown in Fig. 2, the benzoxazole ring of the ligand is parallel and overlapped with the ring of the complex molecule next to the c-axis direction, although its phenylene ring side of the overlapping ligand is above the oxazole side of the original ligand ring, and vice versa. The interplane distance of both ring planes is 3.557 Å. As the thickness of an aromatic ring is about 3.5 Å, these rings are likely in contact with each other. Therefore, some interaction, such as charge transfer, is expected to occur between them. Although there are no coordination bridgings between the complexes, they are thought to be connected in this way, and they are laid in the c-axis direction. As shown in Fig. 2, there is no overlapping of the ligands in the part of the phenolato group as well as the chelate ring; the interatomic distances between the carbon atoms of these parts and of the neighboring ligand are more than 3.5 Å. The central matl parts are lined along the a-axis, although no ligand bridgings exist between them. The barrier of the nonpolar ligand skeleton part is intercalated between the lines of the metal part; thus in the crystal, the polar part and nonpolar part (both of them are parallel to the ab plane) appear alternately.

As shown in Table 2, the equivalent isotropic temperature factor of O(N1) is relatively large. This is probably due to the fact that no atoms approach near to the atom in the crystal: There is a vacancy near the atom, and the atom is not tightly fixed.

As there was no good crystal of the btp complex, **2** to use for X-ray analysis, the single-crystal study has not yet been completed on **2**. But as the powder X-ray pattern of **1** and **2** closely resemble each other, a similar type of structure is expected for the complex **2**.

In their IR spectra, the peaks observed at 1634 cm^{-1} for Hbxp and 1625 cm^{-1} for Hbtp are lowered on chelation to 1612 and 1598 cm^{-1}, respectively. These bands are assigned to the C=N stretching vibration primarily.[16-17] These facts indicate that the coordination takes place through the unsaturated nitrogen atom on the oxazole or thiazole ring. The peaks at 1532, 1318, and 1015 cm^{-1} in the bxp complex and at 1522, 1300, and 1010 cm^{-1} in the btp complex are regarded as the bands of the bidentate nitrate ion. In general, the separation of the two highest frequency bands for the bidentate nitrato complex appears in the range 350—200 cm^{-1},[18] and the separations in **1** and **2** spectra are found to be 214 and 222 cm^{-1} respectively.

The maximum wavenumberes of electronic absorption spectra together with the absorption coefficients (in log ε) of their chloroform solutions are shown in Table 4.

The strong violet color may be caused by a charge-transfer band at 18600 cm^{-1} for the bxp complex and at 18200 cm^{-1} for the btp complex which may occur between very closely overlapped aromatic or pseudo-

Table 4. The Maximum Peak Wavenumbers ($\bar{\nu}$/cm^{-1}) of the Complexes and of the Ligands; Their Absorption Coefficients, log ε, in Parentheses (ε/dm^3 cm^{-1} mol^{-1})

Hbxp	42000 (2.90)	38200 (sh) (3.06)	36600 (3.12)		34100 (3.30)	31300 (3.25)	30100 (3.20)			
$Fe(bxp)_2NO_3$	41300 (4.38)		36400 (4.43)	35000 (4.54)	34100 (4.56)		30100 (4.39)	27800 (sh) (4.13)	23300 (sh) (3.46)	18600 (3.59)
Hbtp	41700 (4.03)	38600 (3.89)		34720 (4.18)	33300 (sh) (4.08)		29900 (4.26)	28900 (sh) (4.21)		
$Fe(btp)_2NO_3$		38800 (4.30)	36000 (sh) (4.45)	34800 (4.50)	33300 (sh) (4.42)		30000 (4.54)	29000 (sh) (4.50)		18200 (3.31)

sh: shoulder.

aromatic rings.[19] Such strong CT bands are also recognized in the salts of tetrahalogenoferate(III) with 3,5-dialkyl-1,2-dithiolium cation.[20,21]

When the violet color solutions of both bxp and btp complexes were left standing for several hours, the color faded away gradually and a brown precipitate was formed.

Magnetic moments were 6.11 BM for the bxp complex and 6.10 BM for the btp complex. Although these values are a little higher than those of the common Fe(III) complexes, there are some other complexes with such high values.[22]

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10) The final anisotropic thermal parameters, and the F_o–F_c table are deposited as Document No. 8753 at the Office of the Editor of Bull. Chem. Soc. Jpn.

11) Key to the symmetry operations: i, 1−x, y, 0.5−z; ii, 1−x, 1−y, 1−x; iii, x, 1−y, 0.5+z.

12) The least-squares plane at the deviation of atoms (l/Å) are as follows.

$$0.1310X - 0.0089Y - 0.9913Z + 2.6808 = 0$$

O(2), 0.0956; O(2^i), −0.0678; O(N2), 0.0795; O(N2^i), −0.1022; Fe, 0.0053,

where

$$\begin{pmatrix} X \\ Y \\ Z \end{pmatrix} = \begin{pmatrix} a & b\cos\gamma & c\cos\beta \\ 0 & b\sin\gamma & -c\cos\alpha^*\sin\beta \\ 0 & 0 & c\cos\alpha^*\sin\beta \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix}.$$

Key to symmetry operation: i, 1−x, y, 0.5−z.

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