Structural and Magnetic Properties of $Cu[C(CN)_3]_2$ and $Mn[C(CN)_3]_2$

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Single-crystal X-ray structure analyses and the measurements of static magnetic susceptibility and ESR have been performed for the title compounds. Crystal data: for $Cu[C(CN)_3]_2$, space group *Pmna*, $a = 7.212(5)$ Å, $b = 5.452(7)$ Å, $c = 10.696(7)$ Å, and $Z = 2$; for $Mn[C(CN)_3]_2$, space group *Pmna*, $a = 7.742(5)$ Å, $b = 5.411(6)$ Å, $c = 10.561(6)$ Å, and $Z = 2$. Both salts are essentially isostructural. The Cu atoms are bridged by two $[C(CN)_3]^-$ anions to form an infinite double chain structure, in which Cu has a square planar coordination ($d_{Cu-N} = 1.986(6)$ Å). The third CN end of the anion is weakly coordinated to the adjacent Cu chain ($d_{Cu-N} = 2.47(1)$ Å), making a three-dimensional network. The crystal is composed of two such interwoven networks. In the Mn complex, the third Mn−N distance (2.256(6) Å) is as short as the equatorial coordinations (2.236(4) Å), so that Mn is coordinated octahedrally. These compounds exhibit paramagnetic behavior following the Curie−Weiss law with Weiss temperatures −1.4 and −9 K, respectively, and the Mn complex undergoes an antiferromagnetic transition at $T_N = 5$ K.

Introduction

Recently polymeric metal complexes have attracted considerable attention because of their intriguing coordination and physical properties.[1] In particular, ferromagnetism at fairly high temperatures has been reported in $M[N(CN)_2]_2$ ($T_c = 9$ K for M = Co and 21 K for M = Ni).[2,3] An analogous organic anion $[C(CN)_3]^-$, which has been called tricyanomethanide or cyanoform anion,[4,5] is one of the simplest ligands which has the ability to form infinite chain or sheet structures. In $Na[C(CN)_3]$ and $K[C(CN)_3]$, the metal ion is coordinated to six nitrogen atoms,[6,7] whereas in $Ag[C(CN)_3]$, the Ag atoms are surrounded by three nitrogen atoms forming a sheet, and two such sheets are interwoven to make a double sheet structure.[8] Preparation of divalent metal complexes has been reported for a long time,[9,10] and a considerable number of their spectroscopic studies have been undertaken.[10−15] However, a brief report concerning the lattice constants and molecular structure of $Cu[C(CN)_3]_2$[16] has not aroused proper attention to the connected crystal structures until recently.[17,18] Furthermore, detailed magnetic measurements using a single crystal have not been undertaken. In the present paper, we describe the crystal structure of $Cu[C(CN)_3]_2$ in comparison with $Mn[C(CN)_3]_2$ and report the measurements of static magnetic susceptibility and ESR. The Cu and Mn salts exhibit anisotropic and isotropic magnetic properties, respectively, in accord with their different coordination environments. The Mn salt undergoes an antiferromagnetic transition at 5 K.

Experimental Section

Synthesis. When an aqueous solution of $K[C(CN)_3]$ was mixed with a solution containing Cu^{2+}, a fine power of $Cu[C(CN)_3]_2$ precipitated immediately.[9] In order to grow large crystals, Cu^+ was used instead of Cu^{2+}. CuCl was suspended in water, and an aqueous solution of $K[C(CN)_3]$ was added. The solution was allowed to stand for several weeks. Cu^+ was gradually oxidized by air, and the water evaporated slowly, to form crystals of $Cu[C(CN)_3]_2$. After the product was washed with water, crystals of $Cu[C(CN)_3]_2$ in the form of brown rods were harvested. The infrared spectra coincided with the previous report.[10]

For $Mn[C(CN)_3]_2$, a warm aqueous solution of $K[C(CN)_3]$ was mixed with a warm aqueous solution of $MnCl_2$, and the resulting solution was allowed to stand for several weeks. After all water evaporated, the product was washed with water, and crystals of $Mn[C(CN)_3]_2$ in the form of colorless truncated octahedra were obtained. These complexes are insoluble either in water or in any ordinary organic solvents.

X-ray Diffraction. The single-crystal X-ray measurements were carried out on a Rigaku Raxis-II Weissenberg-type area detector at room temperature. The structure was solved by the Patterson method, and all atoms were refined anisotropically. Further details are given in Table 1. The computer programs used were a part of teXsan,[19] and neutral atomic scattering factors were taken from *International Tables for X-ray Crystallography*.[20] The final positional parameters are listed in Table 2.

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Table 1. Crystallographic Data for $Cu[C(CN)_3]_2$ and $Mn[C(CN)_3]_2$

	$Cu[C(CN)_3]_2$	$Mn[C(CN)_3]_2$
formula	C_8N_6Cu	C_8N_6Mn
fw	243.674	235.067
space group	*Pmna*	*Pmna*
a, Å	7.212(5)	7.742(5)
b, Å	5.452(7)	5.411(6)
c, Å	10.696(7)	10.561(6)
V, Å^3	420.6(5)	442.5(5)
Z	2	2
ρ_{calcd} g/cm^3	1.924	1.766
μ(Mo Kα), cm^{-1}	25.68	14.04
λ, Å	0.710 70	0.710 70
temp, K	298	298
R^a	0.092	0.065
$R_w{}^b$	0.114	0.083
reflns	464 ($I > 5\sigma(I)$)	605 ($I > 3\sigma(I)$)

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = \{(\sum(w(|F_o| - |F_c|)^2/\sum w|F_o|^2)\}^{1/2}$; *w*: unit weight.

Table 2. Fractional Atomic Parameters of $Cu[C(CN)_3]_2$ and $Mn[C(CN)_3]_2$

atom	*x*	*y*	*z*	$B_{eq}{}^a$/Å^2	occupancy
			$Cu[C(CN)_3]_2$		
Cu	0	$^1/_2$	$^1/_2$	1.25(3)	$^1/_4$
N(1)	0.2006(8)	0.292(1)	0.5699(6)	1.6(1)	1
N(2)	$^1/_2$	−0.260(2)	0.804(1)	2.6(2)	$^1/_2$
C(1)	0.335(1)	0.204(1)	0.6089(7)	1.3(1)	1
C(2)	$^1/_2$	0.102(2)	0.650(1)	1.2(2)	$^1/_2$
C(3)	$^1/_2$	−0.102(2)	0.734(1)	1.5(2)	$^1/_2$
			$Mn[C(CN)_3]_2$		
Mn	0	$^1/_2$	$^1/_2$	0.91(2)	$^1/_4$
N(1)	0.2165(6)	0.2751(9)	0.5799(4)	1.78(8)	1
N(2)	$^1/_2$	−0.269(1)	0.8222(6)	2.1(1)	$^1/_2$
C(1)	0.3451(6)	0.188(1)	0.6160(4)	1.33(8)	1
C(2)	$^1/_2$	0.084(1)	0.6586(6)	1.2(1)	$^1/_2$
C(3)	$^1/_2$	−0.112(1)	0.7474(7)	1.5(1)	$^1/_2$

[a] $B_{eq} = (8/3)\pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2)$.

Magnetic Measurements. The static magnetic susceptibility of a single crystal weighing 1.06 mg for the Cu complex and 0.11 mg for the Mn complex was measured by a Quantum Design SQUID magnetometer MPMS5 under a magnetic field of 1 T between 4 and 300 K. The diamagnetic part was subtracted according to Pascal's law. Since we used a very small single crystal of the Mn complex, the error of the weight was too large to precisely estimate the absolute magnitude of the molar susceptibility. Nevertheless, the observed susceptibilities were consistent with the Cu^{2+} ($S = {}^1/_2$) and Mn^{2+} ($S = {}^5/_2$) spins. The ESR measurements were carried out on an X-band ESR spectrometer JEOL RE200, by using a single crystal.

Results

Crystal Structures. Figures 1 and 2 show the crystal structures of $Cu[C(CN)_3]_2$ and $Mn[C(CN)_3]_2$. The metal atom is located on a 2/*m* site and surrounded by four N(1) atoms in a square planar manner and two N(2) atoms from both sides of the square plane. As shown in Figure 1, two $[C(CN)_3]^-$ anions bridge two metal atoms. The combination of the square planar coordination and the bridged ligands constructs an infinite double chain structure along the crystallographic *a* axis. The third N(2) atom extends toward the adjacent chain, weakly coordinating to the Cu atom. The Cu−N(2) distance, 2.47(1) Å, is significantly longer than the Cu−N(1) distance, 1.986(6) Å, so that the coordination of Cu is approximately regarded as square planar (Table 3). The latter is the usual Cu−N distance in Cu complexes.[1]

$Mn[C(CN)_3]_2$ is basically isostructural with the Cu salt, but the Mn−N(2) distance (2.256(4) Å) is as short as the Mn−N(1) distance (2.236(4) Å). From this the Mn atom has an approximate octahedral coordination. Needless to say, coordination number four is most common for Cu, but six is common for Mn.

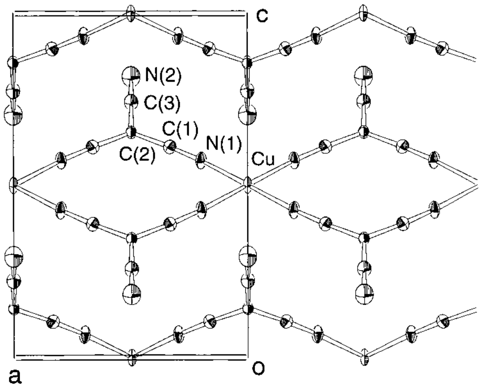

Figure 1. Double-chain structure of $Cu[C(CN)_3]_2$. Thermal ellipsoids are plotted at the 50% probability level.

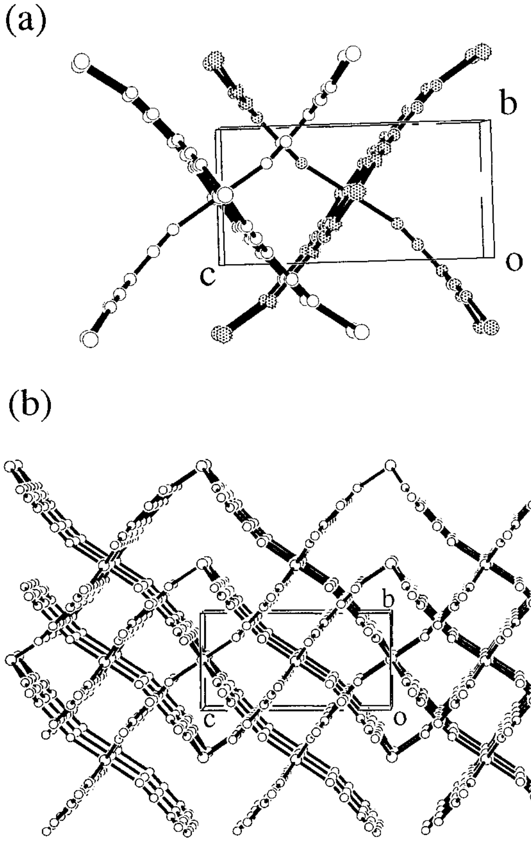

Figure 2. Crystal structure of $Mn[C(CN)_3]_2$, viewed along the *a* axis. (a) Two chain units. (b) Network of the interwoven chain units.

Table 3. Selected Bond Distances (Å) and Angles (deg)

		$Cu[C(CN)_3]_2$			
Cu−N(1)	1.986(6)	Cu−N(2)	2.47(1)	N(1)−C(1)	1.158(9)
C(1)−C(2)	1.384(9)	N(2)−C(3)	1.15(1)	C(2)−C(3)	1.43(1)
N(1)−Cu−N(1)	93.6(3)	Cu−N(1)−C(1)	168.9(5)		
N(1)−C(1)−C(2)	177.0(8)	C(1)−C(2)−C(1)	118.6(8)		
C(1)−C(2)−C(3)	120.7(4)	N(2)−C(3)−C(2)	177(1)		
		$Mn[C(CN)_3]_2$			
Mn−N(1)	2.236(4)	Mn−N(2)	2.256(6)	N(1)−C(1)	1.166(7)
C(1)−C(2)	1.399(6)	N(2)−C(3)	1.161(9)	C(2)−C(3)	1.415(9)
N(1)−Mn−N(1)	97.1(2)	Mn−N(1)−C(1)	169.6(4)		
N(1)−C(1)−C(2)	179.6(5)	C(1)−C(2)−C(1)	118.0(6)		
C(1)−C(2)−C(3)	121.0(3)	N(2)−C(3)−C(2)	178.6(8)		

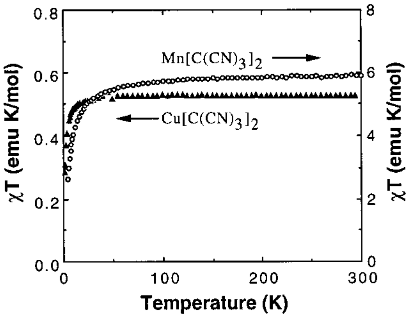

Figure 3. Static magnetic susceptibility, χT plot of $Cu[C(CN)_3]_2$ and $Mn[C(CN)_3]_2$.

These observations agree well with the infrared spectra of $[C(CN)_3]^-$.[10] Enemark and Holm have proposed a polymeric model structure that is the same as Figure 1. From the splitting of the CN stretching in the 2200 cm^{-1} region, they have concluded that the symmetry of $[C(CN)_3]^-$ is nearly D_{3h} but is slightly lower than this symmetry. The present X-ray result indicates C_{2v} symmetry, which is in agreement with the observed spectra. The infrared spectra show larger splitting in the Cu complex than the Mn complex. This is associated with the large difference in the Cu−N(1) and the Cu−N(2) distances. The electronic spectra support the nearly octahedral coordination of the metal atoms as well. From the spectral similarities, other Fe, Co, and Ni complexes are considered to be isostructural.

As shown in Figure 2a, there are two kinds of double chains; one is located on $(x, 0, {}^1/_2)$, and the other is on $(x, {}^1/_2, {}^1/_2)$. These two chains are designated by open and shaded atoms in Figure 2a. In these two chains, the planes of the double chains are tilted in different directions. Because these two are shifted by a half unit cell along the *a* axis, the CN(2) unit of one chain extends outward by passing between the two CN(2) units of the other chain (Figure 1) and coordinates to the adjacent chain. Accordingly a square-lattice-like network is formed, as shown in Figure 2b. This brings about two kinds of networks, one of which includes the chain on $(x, 0, {}^1/_2)$, and the other contains that on $(x, {}^1/_2, {}^1/_2)$. Even if we trace these two networks to infinity, there is no chemical bond between them. Nonetheless, these two networks are interwoven with each other and are never separable without breaking some chemical bonds.

Inclusion of water like $M[C(CN)_3]_2(H_2O)_x$ ($x = 0.25-0.5$) has been suggested from the elemental analyses for Fe, Co, and Ni,[9] and from the infrared spectra for all metal complexes (Mn−Cu).[10] We have not, however, found any appropriate site for the water molecule, and the refinement including an oxygen atom has diverged. We have to conclude that there is no water molecule included in the present crystals.

Magnetic Susceptibility. Static magnetic susceptibility of $Cu[C(CN)_3]_2$ and $Mn[C(CN)_3]_2$ is shown in Figure 3. The temperature dependence basically follows the Curie−Weiss law, where the Weiss temperatures are −1.4 and −4.8 K, respectively. The Weiss temperature of the Cu complex is low, and no magnetic transition has been observed. The χT plot of the Mn complex (Figure 3) shows a significant drop at low temperatures, suggesting a comparatively strong antiferromagnetic interaction. The drop is, however, gradual, and a magnetic transition is not clearly observed.

ESR. The ESR line shape of $Cu[C(CN)_3]_2$, measured at room temperature, is depicted in Figure 4. When the magnetic field is applied along the crystallographic *a* axis, the line is composed of a single Lorentzian. On the contrary, when the field is applied in the $b + c$ direction, a complicated line shape has been observed. The line shape is, however, fitted with a sum of two Lorentzian functions, as shown in Figure 4. If the field is rotated within the *bc* plane, the centers of the two peaks, i.e., the *g* values, exhibit an angle dependence as shown in Figure 5. This angle dependence is composed of two independent sine curves. From this fitting, we can obtain the principal *g* values as $g_1 = 2.335$ and $g_2 = 2.102$. The *g* value along the *a* axis is $g_a = 2.082$. The two Lorentzian peaks within the *bc* plane correspond to the two kinds of double chains which have two different orientations. The principal $g_2 = 2.102$ is very close to $g_a = 2.082$. These values correspond to the values when the field is applied within the coordination plane; this agrees with the nearly square planar coordination. By contrast $g_1 = 2.335$ originates from the *g* value when the field is applied perpendicular to the coordination plane. These principal *g* values are in good agreement with those from a square planar Cu^{2+}. When the field is rotated within the *bc* plane, the two peaks coincide at $H \| b$ and $H \| c$.

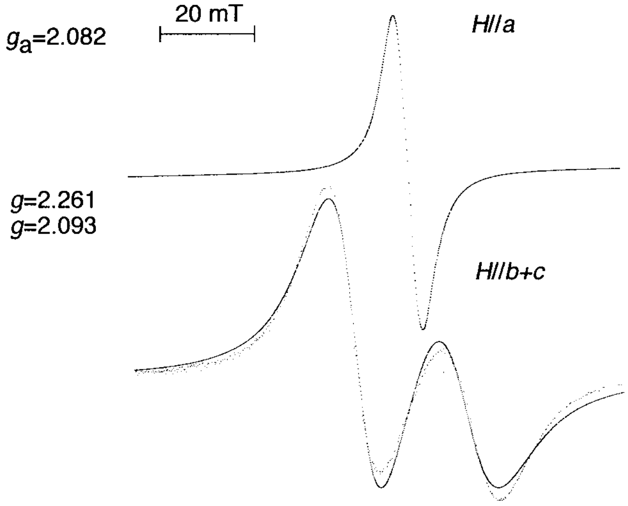

Figure 4. ESR line shape in $Cu[C(CN)_3]_2$ at room temperature for $H \| a$ and approximately $H \| b + c$.

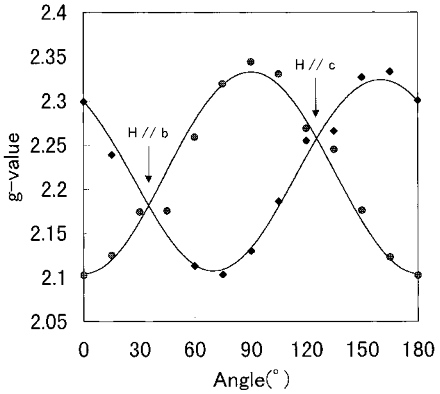

Figure 5. ESR angle dependence of *g*-values in $Cu[C(CN)_3]_2$ at room temperature.

The temperature dependence has been measured along $H \| a$ (Figure 6), because the line shape is a single Lorentzian in this direction. The line width is about 1.0 mT at room temperature and gradually decreases at low temperatures. The intensity basically obeys the Curie−Weiss law, so that in Figure 6 the inverse of the intensity is plotted. From the low-temperature part, the Weiss temperature is estimated to be 0.18 K; this small value indicates weak magnetic interaction.

The ESR spectrum of $Mn[C(CN)_3]_2$ is composed of a single Lorentzian in all directions, and the anisotropy of the *g* value is very small ($g_{max} = 2.019$ and $g_{min} = 2.017$ at room

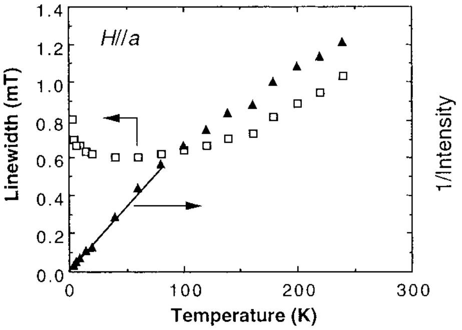

Figure 6. Temperature dependence of ESR line width and inverse intensity in $Cu[C(CN)_3]_2$.

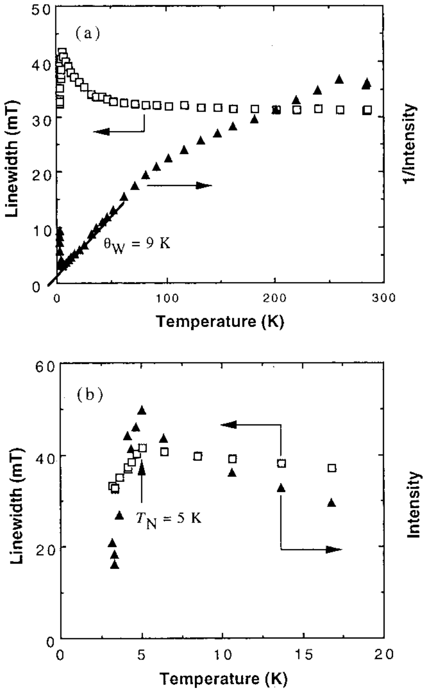

Figure 7. (a) Temperature dependence of ESR line width and inverse intensity in $Mn[C(CN)_3]_2$. (b) Low-temperature part of the same experiment. The intensity is plotted instead of the inverse intensity.

temperature). This is in agreement with the isotropic coordination of the Mn complex. Figure 7 shows the temperature dependence of the line width and the ESR intensity. The line width is very large, 30 mT, but is approximately temperature independent down to low temperatures. The intensity obeys the Curie−Weiss law, though the gradient changes around 100 K. From the low-temperature region, the Weiss temperature is estimated to be 9 K. The intensity attains a maximum at 5 K, below which the intensity drops abruptly. At the same time, the line width sharpens. In view of the comparatively high Weiss temperature, this is most likely an antiferromagnetic transition.

In the SQUID measurement of field dependence of the magnetization M at 2 K, M/H drops below 150 mT, indicating a spin-flip transition at this field. This proves antiferromagnetic order of the magnetic phase. Because the exchange field H_E is estimated to be 35 T from the Weiss temperature, the anisotropy field H_A is obtained to be 0.3 mT. The very small anisotropy $H_A/H_E = 10^{-5}$ indicates the Heisenberg nature of the spin system, in agreement with the isotropic coordination environment.

Discussion

Intriguing conducting and magnetic properties have been reported in $Cu(DMDCNQI)_2$ (DMDCNQI: dimethyl-*N*,*N*′-dicyanoquinonediimine) and the related materials.[21] In these compounds, the CN parts of the DCNQI molecules coordinate to the Cu atoms, which are then bridged to form a three-dimensional network. The fractional charge on $DCNQI^{2/3-}$ mediates the good electric conduction and the significant magnetic interaction (Neel temperatures around 10 K). By contrast, the present $[C(CN)_3]^-$ has a closed-shell system, resulting in no electric conduction and the comparatively weak magnetic interaction.

Nevertheless there is something common from the structural point of view. $[C(CN)_3]^-$ has three CN parts, and the composition is 1:2. Then there are six CN groups per Cu atom. The coordination number of Cu is actually six. DCNQI has two CN, and the composition is 1:2, so that the coordination number is four. In a similar manner, Cu(TCNQ) (TCNQ: tetracyanoquinodimethane) is a 1:1 complex, and TCNQ has four CN parts, resulting in coordination number four.[22,23] These examples indicate that there remains no unused CN group. This seems to be an important requirement when these polycyanocarbons make metal complexes with an infinite network.

Since $[C(CN)_3]^-$ is one of the simplest bridging ligands, it is interesting to discuss the metal dependence of the magnitude of the magnetic interaction. In the Cu complex, the unpaired electron is located on the $d_{x^2-y^2}$ orbital. Since this orbital is oriented toward the N(1) atoms, making σ-like bonds with the ligands, this orbital is orthogonal to the ligand π orbitals. As a result, the Weiss temperature is low (<1 K). By contrast, the unpaired electrons of the Mn complex are incorporated in all kinds of the d orbitals, particularly in t_{2g} orbitals. Because the t_{2g} orbitals make π bonds with the ligand π orbitals, the magnetic interaction is comparatively strong. This is the origin of the relatively large Weiss temperature (9 K) and the antiferromagnetic transition at 5 K.

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Supporting Information Available: Four X-ray crystallographic files, in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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