

atives of metal carbonyls have, however, been previously reported.³ Furthermore, these are the first examples of complexes in which there exist molybdenum-selenium and molybdenum-tellurium bonds.

Mononuclear complexes of the type $\pi\text{-CpMo}(\text{CO})_3\text{X}$ ($\text{X} = \text{H}$, halogen, CH_3 , $\text{Sn}(\text{C}_6\text{H}_5)_3$, etc.) are well known, and the volatility, low melting points, and infrared spectra of $\pi\text{-CpMo}(\text{CO})_3\text{EC}_6\text{H}_5$ ($\text{E} = \text{Se}$, Te) are as expected for compounds of this type. It is of interest that the highest energy carbonyl stretching absorptions in the complexes $\pi\text{-CpMo}(\text{CO})_3\text{X}$ are 2055, 2049, 2040, 2033, 2026, and 2016 cm^{-1} for $\text{X} = \text{Cl}$,⁷ Br ,⁷ I ,⁷ SC_6H_5 , SeC_6H_5 , and TeC_6H_5 , respectively. These data suggest that π bonding between molybdenum and carbon monoxide is strongest in the tellurium complex, and the stabilities of $\pi\text{-CpMo}(\text{CO})_3\text{EC}_6\text{H}_5$ ($\text{E} = \text{S}$, Se , Te) as observed in the preparative experiments indicate that the ability of the chalcogen to stabilize the mononuclear species decreases in the order of E : $\text{Te} > \text{Se} > \text{S}$. Thus the greater "softness" of tellurium and selenium relative to sulfur results in a less positive charge on the molybdenum, and π bonding to CO is thereby enhanced. Decomposition of $\pi\text{-CpMo}(\text{CO})_3\text{EC}_6\text{H}_5$ by loss of carbon monoxide to form $[\pi\text{-CpMo}(\text{CO})_2\text{EC}_6\text{H}_5]_2$ therefore decreases in the order of E : $\text{S} > \text{Se} > \text{Te}$.

As noted in the Results section, the only dinuclear complex of the type $[\pi\text{-CpMo}(\text{CO})_2\text{EC}_6\text{H}_5]_2$ which was isolated and characterized was that for $\text{E} = \text{Te}$. The selenium analog was undoubtedly present in the reaction mixtures, but the sulfur analog was not detected. Thus, as with the mononuclear derivatives, the gross stability of the dinuclear species may be correlated with the "softness" of the chalcogen donor atom. The infrared spectra of $[\pi\text{-CpMo}(\text{CO})_2\text{EC}_6\text{H}_5]_2$ ($\text{E} = \text{Te}$, Se) show four bands in the carbonyl stretching region and are similar to the reported spectrum of $[\pi\text{-CpMo}(\text{CO})_2\text{SCH}_3]_2$.⁸ A similar structure with $\text{C}_6\text{H}_5\text{E}$ bridging units is proposed.⁹ Although several geometrical isomers may be envisioned for $[\pi\text{-CpMo}(\text{CO})_2\text{TeC}_6\text{H}_5]_2$, the NMR spectrum shows only one kind of cyclopentadienyl proton.

Prolonged reaction of $(\text{C}_6\text{H}_5)_2\text{E}_2$ ($\text{E} = \text{S}$, Se , Te) with $[\pi\text{-CpMo}(\text{CO})_3]_2$ gave highly insoluble materials whose elemental analyses suggest the formulation $[\pi\text{-CpMo}(\text{EC}_6\text{H}_5)_2]_x$. The nature of these compounds has prevented a determination of the value of x in the formula.

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Coordination Compounds of Thallium(III).

V. The Vibrational Spectra of Mixed Tetrahalothallates of the Type

$(\text{C}_2\text{H}_5)_4\text{NTlX}_{4-n}\text{Y}_n$, where $n = 1, 2$, or 3

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The complete series of tetrahalothallates of the type $(\text{C}_2\text{H}_5)_4\text{NTlX}_{4-n}\text{Y}_n$, where $\text{X} = \text{Cl}$ when $\text{Y} = \text{Br}$ or I and $\text{X} = \text{Br}$ when $\text{Y} = \text{I}$, and $n = 1, 2$, or 3 , have recently been synthesized^{1,2} and shown¹ from X-ray powder data and electronic absorption spectra measurements to contain the authentic $\text{TlX}_{4-n}\text{Y}_n^-$ species. This has provided an ideal opportunity to investigate in detail the vibrational spectra of a complete series of tetrahedral anions of the type $\text{MX}_{4-n}\text{Y}_n^-$. To date, no such investigation appears to have been reported, although the far-infrared spectra of the related zinc(II) anions (except $\text{ZnCl}_3\text{I}^{2-}$) have recently been described.³ The tetrahalothallates are particularly suitable for such an investigation since they are air stable and very soluble in acetonitrile, an ideal spectroscopic solvent below 380 cm^{-1} , thus facilitating polarization measurements and providing a useful check on the possibility that some absorption bands might arise from solid-state effects.

The spectra of the TlCl_3I^- (infrared and Raman) and TlCl_3Br^- (infrared) anions have been reported in an earlier paper.² These results are compared with those described in the present report for the remaining mixed-halo species, as are the literature data for the TlCl_4^- , TlBr_4^- , and TlI_4^- anions.⁴

Experimental Section

The preparation of the complexes has been described previously.^{1,2} The samples used in the present spectroscopic investigation were those whose analytical data, X-ray powder photographs, and electronic absorption spectra have already been measured.^{1,2}

Raman spectra were recorded on a Cary 81 spectrophotometer equipped with an He-Ne laser source. The characteristics of this particular instrument have been described elsewhere.⁵ Good-quality spectra of the crystalline solids were obtained with the sample contained in a stoppered Pyrex tube. Solution measurements were carried out on saturated acetonitrile solutions of several of the complexes. Infrared spectra were recorded on Nujol mulls using a Beckman IR-11 infrared spectrophotometer in the region 350–33 cm^{-1} .

Results and Discussion

Complex Anions TlX_3Y^- and TlXY_3^- .—Data for these particular anions are listed in Table I, and assignments

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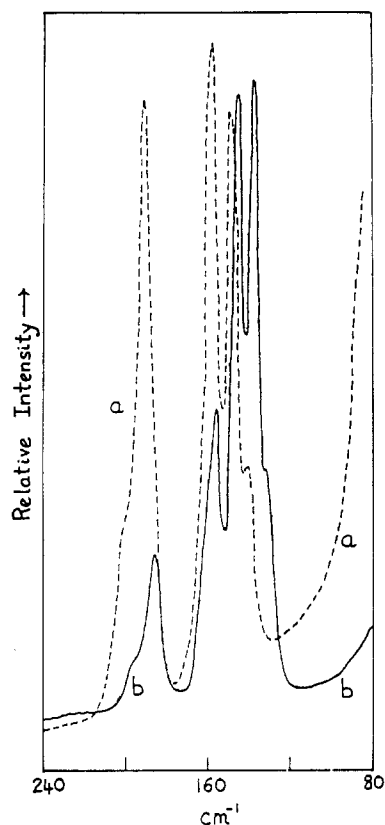


Figure 1.—The Raman spectra of (a) crystalline $(C_2H_5)_4NTlBr_3I$ (sensitivity, 2×20 ; slit width, 5 cm^{-1}) and (b) crystalline $(C_2H_5)_4NTlBr_3I_2$ (sensitivity, 20; slit width, 5 cm^{-1}).

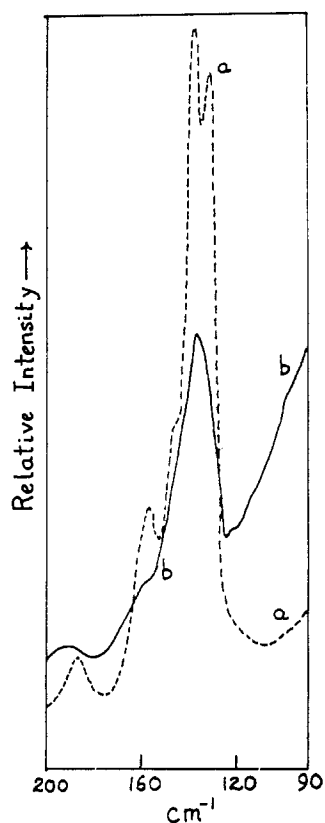


Figure 2.—The Raman spectra of $(C_2H_5)_4NTlI_3Br$: (a) crystals (sensitivity, 2×20 ; slit width, 5 cm^{-1}); (b) acetonitrile solution (sensitivity, 200; slit width, 10 cm^{-1}).

of the thallium-halogen stretching modes are shown in Table II. Several Raman spectra are illustrated in Figures 1 and 2.

TABLE I
VIBRATIONAL FREQUENCIES ($350\text{--}33 \text{ cm}^{-1}$) OF THE TlX_4^- ,
 TlX_3Y^- , AND $TlX_2Y_2^-$ ANIONS

Anion ^a	Medium ^b	Spec- trum ^c	M-X, M-Y, and lattice vibrations, ^d cm^{-1}
$TlCl_3Br^-$	Solid	R	307 s, 296 sh, 202 s, ~ 97 sh
$TlCl_3I^-$	CH_3CN	R	308 sh (p?), 302 ms (p), 288 sh (d), 168 s (p), 153 s (p), 143 w (?), 111 sh (d?)
$TlBr_4^-$	NM	I	200 s, 93 ms
	Solid	R	196 sh, 186 s, ~ 86 sh?
$TlBr_3Cl^-$	NM	I	290 s, 200 s, 98 m, 72 sh, ~ 48 sh?
	Solid	R	293 mw, ~ 200 sh, 193 s, 188 s, 83 sh, 72 sh
$TlBr_3I^-$	NM	I	200 s, 160 m, 87 ms
	Solid	R	~ 200 sh, 187 s, 156 s, 147 s, 140 w
	CH_3CN	R	205 sh (d), 194 s (p), 161 s (p), 149 s (p), 138 sh (?)
TlI_4^-	NM	I	152 s, 72 mw
	Solid	R	154 s, 130 s
TlI_3Cl^-	NM	I	271 s, 156 s, 136 sh, 88 m, ~ 70 sh, ~ 55 sh
	Solid	R	276 vw, 259 vw, 152 w, 140 mw, 130 vs, ~ 84 w?
TlI_3Br^-	NM	I	186 s, 158 s, 80 ms
	Solid	R	187 w, 156 m, 145 sh, 138 s, 131 s, 81 sh
	CH_3CN	R	192 w (p), 160 sh (d), 137 s (p)
$TlCl_2Br_2^-$	NM	I	292 vs, br, 204 s, 104 ms, ~ 72 sh?, ~ 52 sh
	Solid	R	299 ms, 291 sh, 199 s, 193 s, ~ 100 m, br, ~ 80 w?
$TlCl_2I_2^-$	NM	I	280 vs, br, 160 ms, 137 w, 98 m
	Solid	R	~ 290 sh?, 280 w, br, 163 w, 151 s, 140 vs, 131 s, ~ 75 sh
	CH_3CN	R	~ 286 w (d), ~ 165 (d), 152 ms (d?), 142 s (p), 133 w (d?)
$TlBr_2I_2^-$	NM	I	196 s, 161 ms, 144 sh, ~ 88 m, ~ 36 mw?
	Solid	R	196 vw, 186 mw, 154 m, 144 s, 136 s, 130 w, ~ 83 sh
	CH_3CN	R	198 sh (d), 193 m (p), 159 m (d), 148 s (p), 141 s (p)

^a Additional data for the $TlCl_3Br^-$ and $TlCl_3I^-$ anions given in ref 2. ^b NM = Nujol mull. ^c R = Raman; I = infrared. ^d Figures in parentheses refer to polarization measurements: p, polarized; d, depolarized.

As the molecular symmetry of a four-coordinate species is lowered from T_d to C_{3v} , so $A_1 \rightarrow A_1$, $E \rightarrow E$, and $F_2 \rightarrow A_1 + E$.⁶ In C_{3v} symmetry, the six modes of such a pseudo-tetrahedral species are infrared and Raman active (Table II).

Previous work has shown^{2,4} that the thallium-halogen bending modes of the tetrahedral TlX_4^- species, where X = Cl, Br, or I, occur below 100 cm^{-1} , so that the related modes of $TlX_{4-n}Y_n^-$ are unlikely to hinder our assignments of $\nu(Tl-X)$. For the latter species, considerable uncertainty exists in the unambiguous assignment of $\delta(Tl-X)$ and $\delta(Tl-Y)$. Most of the complexes show bands below 120 cm^{-1} which arise

(6) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, Inc., New York, N. Y., 1963, p 111.

TABLE II
 VIBRATIONAL ASSIGNMENTS^a OF THE TlX_4^- AND TlX_3Y^- ANIONS

Anion	Medium	Spectrum	$\text{TlX}_4^- (\text{T}_d)$					
			$A_1(\text{R})$ $\nu_8(\text{TlX})$	$E(\text{R})$ $\delta_d^a(\text{XTlX})$	$F_2(\text{I, R})$ $\nu_d(\text{TlX})$		$F_2(\text{I, R})$ $\delta_d(\text{XTlX})$	
			$A_1(\text{I, R})$ $\nu(\text{Tl-Y})$	$E(\text{I, R})$ $\delta(\text{XTlX})$	$A_1(\text{I, R})$ $\nu(\text{TlX})$	$E(\text{I, R})$ $\nu_d(\text{TlX})$	$A_1(\text{I, R})$ $\delta(\text{TlX})$	$E(\text{I, R})$ $\rho_r(\text{TlX}_3)$
TlCl_4^- ^b	310	60	296			(108-80)
TlCl_3Br^-	NM	I	204	292	106	...
	Solid	R	202	...	307	296	~97	...
TlCl_3I^-	NM	I	164 or 152	283	106	...
	Solid	R	164 or 151	...	302?	282	97	...
	CH_3CN	R	168 or 153	...	291			
					308?	288	111	...
					302			
TlBr_4^-	NM	I	200	93	...
	Solid	R	186	196	86	...
TlBr_3Cl^-	NM	I	290	200	98	72
	Solid	R	293	...	193	~200	83	72
					188			
TlBr_3I^-	NM	I	160	200
	Solid	R	156 or 147	200
	CH_3CN	R	161 or 149	...	194	205
TlI_4^-	NM	I	152	72?	...
	Solid	R	130	154
TlI_3Cl^-	NM	I	271	...	136	156	88	...
	Solid ^c	R	276	...	130	152	84	...
TlI_3Br^-	NM	I	186	158	80	...
	Solid	R	187	...	138	156	81	...
					131			
	CH_3CN	R	192	...	137	160

^a Taken from K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, Inc., New York, N. Y., 1963, p 111. ^b Data taken from ref 2 and 4.

 TABLE III
 ASSIGNMENTS OF THE THALLIUM-HALOGEN STRETCHING
 VIBRATIONS OF THE TlX_2Y_2^- ANIONS

Anion	Medium	Spec- trum	$\nu(\text{Tl-X}), \text{cm}^{-1}$		$\nu(\text{Tl-Y}), \text{cm}^{-1}$	
			B_2	A_1	B_1	A_1
$\text{TlCl}_2\text{Br}_2^-$	NM	I	292	...	204	...
	Solid	R	299	291	199	193
$\text{TlCl}_2\text{I}_2^-$	NM	I	280	...	160	137
	Solid	R	290	280	163	140
	CH_3CN	R	286	...	165	142
$\text{TlBr}_2\text{I}_2^-$	NM	I	196	...	161	144
	Solid	R	196	186	154	144
						136
	CH_3CN	R	198	193	159	148
						141

either from these bending modes or from lattice modes. The assignment of a band in several of the complexes to $\delta(\text{Tl-X})$ of A_1 symmetry (Table II) must be regarded as tentative. Since the absorption bands arising from these modes are of less diagnostic value than $\nu(\text{Tl-X})$ and $\nu(\text{Tl-Y})$, they are not considered further in the present work.

The vibrational spectra of $(\text{C}_2\text{H}_5)_4\text{NTlBr}_4$ and $(\text{C}_2\text{H}_5)_4\text{NTlI}_4$ were also investigated so that the data for the TlX_4^- and $\text{TlX}_{4-n}\text{Y}_n^-$ anions could be compared when they were stabilized by the same cation (Table II). ν_1 , ν_3 , and ν_4 for $(\text{C}_2\text{H}_5)_4\text{NTlBr}_4$ and $(\text{C}_2\text{H}_5)_4\text{NTlI}_4$ are in good agreement with the corresponding modes assigned for other salts containing these anions,⁴ although ν_4 for TlBr_4^- is at a slightly higher frequency (by up to 20 cm^{-1}) than noted by Spiro.⁴ For neither of the above salts was ν_2 , the E bending mode, located.

The assignments for the TlCl_3Br^- and TlI_3Cl^- anions are straightforward, although $\nu(\text{Tl-Cl})$ of A_1 symmetry was not observed in the infrared spectrum of the former anion. For TlBr_3Cl^- and TlI_3Br^- a splitting of the bands assigned to $\nu(\text{Tl-Cl})$ and $\nu(\text{Tl-Br})$, respectively, is noted in the solid-state Raman spectra. The small magnitude of this split—ca. 5 and 8 cm^{-1} , respectively—and the observation that $\nu(\text{Tl-Br})$ is not split in the Raman spectrum of an acetonitrile solution of TlI_3Br^- imply that this band splitting arises from a *solid-state* effect.

Whereas the infrared spectra of TlCl_3I^- and TlBr_3I^- are as expected, their Raman spectra, both in the solid state and in acetonitrile, have two intense polarized bands in the region where a single absorption of A_1 symmetry, assignable to $\nu(\text{Tl-I})$, is anticipated. This feature of the Raman spectrum of crystalline $(\text{C}_2\text{H}_5)_4\text{NTlCl}_3\text{I}$ has been noted previously² but remained unexplained. For both of these anions contamination by TlI_4^- can be ruled out since an equally intense band at $\sim 130 \text{ cm}^{-1}$ must be present if this species is present as an impurity. It is also clear that these "extra" bands do not arise from solid-state effects. Two further possibilities which seem more likely are (a) that the additional bands are due to contamination by other mixed-halo species or (b) that they are due to overtone or combination bands with enhanced intensity, presumably by Fermi resonance, from the $A_1 \nu(\text{Tl-I})$ modes of TlCl_3I^- or TlBr_3I^- .

Both of the above anions also show a weak absorption at $\sim 140 \text{ cm}^{-1}$ (Table I) and very weak depolarized

bands at ~ 160 and 164 cm^{-1} , respectively. The latter would normally be obscured by the intense polarized bands at $\sim 165\text{ cm}^{-1}$. It is concluded that these *weak* bands are due to trace amounts of $\text{TlCl}_2\text{I}_2^-$ and $\text{TlBr}_2\text{I}_2^-$, respectively (see Table III). Since electronic absorption spectral measurements and X-ray powder photographs¹ give no evidence for significant contamination by these impurities, we conclude that the high intensity of the twin bands in the $170\text{--}145\text{-cm}^{-1}$ region, both in the solid state and solution, rules out the possibility that either of them arises from impurities. The only remaining conclusion is that they result from combination or overtone vibrations, a possibility mentioned earlier. For the TlCl_3I^- anion, a band at $\sim 77\text{ cm}^{-1}$ in the infrared spectrum² gives some support to this postulate since the first overtone of this band could account for the band doubling.

At this point it may be noted that Deacon, *et al.*,³ have recently found that in the infrared spectra of $[(\text{C}_2\text{H}_5)_4\text{N}]_2\text{ZnX}_3\text{Y}$, where $\text{X} = \text{I}$ when $\text{Y} = \text{Br}$ and $\text{X} = \text{Br}$ when $\text{Y} = \text{I}$, two $\nu(\text{Zn}-\text{Y})$ modes are observed although symmetry requires only one. No satisfactory explanation is yet available for this band doubling.

Complex Anions TlX_2Y_2^- .—A further increase in the complexity of the spectra of pseudo-tetrahedral $\text{TlX}_{4-n}\text{Y}_n^-$ should result as the symmetry is lowered from C_{3v} to C_{2v} . In particular, four thallium-halogen stretching modes (symmetry $2\text{A}_1 + \text{B}_1 + \text{B}_2$) are predicted in both the infrared and Raman spectra. From the spectral data available for the $\text{TlCl}_2\text{Br}_2^-$, $\text{TlCl}_2\text{I}_2^-$, and $\text{TlBr}_2\text{I}_2^-$ anions (Tables I and III), this prediction is usually realized, although a clear resolution of the two $\nu(\text{TI}-\text{X})$ and $\nu(\text{TI}-\text{Y})$ modes is not always observed in the infrared spectra.

The Raman spectrum of $\text{TlCl}_2\text{I}_2^-$ (Table I) reveals bands at 152 and 133 cm^{-1} which could be attributed to TlI_4^- impurity, although the latter was not detected in the electronic absorption spectrum¹ of this sample. Polarization measurements revealed a broad depolarized band centered at $\sim 157\text{ cm}^{-1}$. This band envelope probably contains $\nu_d(\text{TI}-\text{I})$ of $\text{TlCl}_2\text{I}_2^-$ (165 cm^{-1}) and ν_3 of TlI_4^- (154 cm^{-1}).

From the Raman spectrum of crystalline $(\text{C}_2\text{H}_5)_4\text{N}\text{TlBr}_2\text{I}_2$ it is uncertain whether the A_1 mode $\nu(\text{TI}-\text{I})$ is at 146 or 138 cm^{-1} . This band doubling is similar to that described previously for TlCl_3I^- and TlBr_3I^- .

No attempt has been made to assign in detail the five deformation modes of a TlX_2Y_2^- molecule of C_{2v} symmetry.

Concluding Remarks.—From the preceding section it has been shown that the products of stoichiometry $(\text{C}_2\text{H}_5)_4\text{N}\text{TlX}_{4-n}\text{Y}_n$, where $n = 1, 2,$ or 3 , are pure phases and not mixtures of the appropriate TlX_4^- and TlY_4^- anions. Occasionally there is evidence, particularly from the Raman measurements, that the products contain trace amounts of other tetrahalothallate impurities. This incidentally reflects the difficulty of purifying the complexes by recrystallization, since all these salts have very similar solubility properties.

In agreement with the work of Deacon, *et al.*,³ on the related mixed tetrahalozincate(II) anions, we conclude that the far-infrared spectra of such species, in contrast to their Raman spectra, are relatively unhelpful in unambiguously establishing their detailed stereochemistry, although such measurements can be used to confirm that the products are not mixtures of the component tetrahalometalates.

The origin of the "band doubling" observed for several of the tetrahalothallates remains obscure and it will be interesting if such effects can be detected in related systems.

Finally, while it is clear that $\text{TlX}_{4-n}\text{Y}_n^-$ can be stabilized in the solid state this need not be the case in solution. Thus it might have been anticipated that when TlX_3Y^- , for example, was dissolved in acetonitrile, equilibrium amounts of the species TlX_2Y_2^- , TlX_4^- , etc., would be formed. However, the very close similarity of the solid and solution Raman spectra gives no definite evidence for such equilibria in the systems investigated, so, if equilibria are established, they must favor the parent $\text{TlX}_{4-n}\text{Y}_n^-$ species which is dissolved. Also, the similarity of the solid and solution Raman spectra would seem to rule out the formation of significant amounts of polynuclear halide-bridged species such as $\text{Tl}_2\text{X}_{9-n}\text{Y}_n^{3-}$. However, these conclusions from the solution measurements cannot be regarded as entirely unambiguous.

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The Lattice Parameters of a Series of Mixed Hexabromides

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The group of salts of the type A_2SbX_6 ($\text{A}^+ = \text{NH}_4^+$, Rb^+ , or Cs^+ ; $\text{X}^- = \text{Cl}^-$ or Br^-) have been investigated by several workers^{1,2} primarily in an attempt to see if the antimony is present in a tetravalent state or as a mixture of trivalent and pentavalent states and to explain the cause of the characteristic black color of these hexahalides in terms of the oxidation state(s). In general, these salts crystallize in a tetragonal, pseudo-cubic unit cell, and from the value of the axial ratio, c/a , a quantitative estimate of the deviation from cubic symmetry has been obtained.

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