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¹H NMR Study of Aziridine Derivatives Coordinated to the Paramagnetic Undecatungstocobalto(II)silicate and -nickelo(II)silicate Anions

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¹H NMR spectra of D_2O solutions containing 2,2-dimethylaziridine (1) or 2-methylaziridine (2) and [SiW$_{11}$Co^{II}O$_{39}$]$^{6-}$ (SiW$_{11}$Co) or [SiW$_{11}$Ni^{II}O$_{39}$]$^{6-}$ (SiW$_{11}$Ni) exhibit separate signals for the free ligand and the complex, indicating that the ligand exchange is slow on the NMR time scale. Identified are two linkage isomers with the methyl group of **2** at *trans* or *cis* position with respect to the metal. The isotropic shifts of **1** and **2** coordinated to SiW$_{11}$Ni originate mainly from the contact shifts, and they agree reasonably with the relative values reported for similar ligands coordinated to bis(2,4-pentanedionato)nickel(II). The isotropic shifts for the SiW$_{11}$Co complexes were separated into contact and pseudocontact contributions. The pseudocontact shifts show that $(\chi_\parallel - \chi_\perp)$ is positive, while that for the SiW$_{11}$Co complexes of pyridine derivatives is negative. This result indicates that the ordering of d_{xy} and d_{xz}, d_{yz} orbitals in SiW$_{11}$Co complexes can be reversed by ligands.

Introduction

Several years ago we discovered that the exchange rates of some ligands coordinated to a Co^{2+} ion could be varied by incorporating it in various polyoxometalates.[1,2] It has been shown that pyridine- and imidazole-type ligands coordinated to [SiW$_{11}$CoO$_{39}$]^6 (SiW$_{11}$Co) or [SiW$_{11}$NiO$_{39}$]$^{6-}$ (SiW$_{11}$-

Ni) undergo slow exchange on the NMR time scale, exhibiting separate signals for the complexes and the free ligands in their ¹H and ¹³C NMR spectra.[1,2] Well-resolved NMR spectra of various ligands coordinated to paramagnetic polyoxometalates can provide useful information on both the ligands and polyoxometalates.[3,4]

The isotropic NMR shifts (δ_{iso}) in a paramagnetic system

contain contributions from contact (δ_{con}) and pseudocontact shifts (δ_{dip}).

$$\delta_{iso} = \delta_{con} + \delta_{dip} \tag{1}$$

Contact shifts occur when unpaired electron density is transferred from the metal to the ligand nucleus in question, whereas pseudocontact shifts arise from a through-space dipolar interaction between the electronic and nuclear magnetic moments.[5]

Since the contact shifts contain contributions from both σ- and π-electron delocalizations for pyridine and imidazole derivatives, it is difficult to separate the isotropic shifts into three components. So we have studied ^{1}H NMR spectra of aziridine derivatives coordinated to SiW$_{11}$Co and SiW$_{11}$Ni, which are σ-electron systems. Analysis of the isotropic shifts shows that (χ -χ) is positive for the SiW$_{11}$Co complexes of aziridine derivatives, while it is negative for the SiW$_{11}$Co complexes of pyridine derivatives.

^{1}H NMR data for sixty-four aziridine derivatives are given in the literature,[6] but the data for 2,2-dimethylaziridine (1) and 2-methylaziridine (2) are not included. ^{1}H NMR spectra of 1 and N-alkylaziridine coordinated to bis(2, 4-pentanedionato)nickel(II) were briefly described before.[7] But these systems exhibited averaged NMR spectra for the free ligands and the complexes, for the ligand exchange was fast on the NMR time scale.

Experimental

K$_6$[SiW$_{11}$Co(H$_2$O)O$_{39}$]·nH$_2$O and K$_6$[SiW$_{11}$Ni(H$_2$O)O$_{39}$]·nH$_2$O were prepared according to the methods of Simmons[8] and Weakley *et al.*[9] 2-Methylaziridine was purchased from Aldrich, and 2,2-dimethylaziridine was synthesized according to the literature method.[10] D$_2$O solutions were prepared ~0.02 M in each of a ligand and a polyoxometalate.

^{1}H NMR spectra were obtained in the Fourier transform mode with Varian Gemini-300 and 200 spectrometers equipped with broad bands, narrow-bore probes. NMR measurements were made at ambient temperature (22-25 °C). The line-broadening factor used in exponential apodization was 20 Hz. Pulses of 90° (10 μs) were used, and the acquisition time was 0.2 s. No extra delay time was introduced between pulses. The residual water resonance in each spectrum was saturated by irradiating with a single frequency pulse which was gated off during acquisition. Sodium salt of 3-(trimethylsilyl)propionic-2,2,3,3-d$_4$ acid (TSP) was used as an internal reference.

Results and Discussion

2,2-Dimethylaziridine. The ^{1}H NMR spectrum of 1 in CDCl$_3$ exhibits two sharp peaks at 1.54 and 1.22 ppm with an intensity ratio of 1:3, which are assigned to the ring protons and the CH$_3$ groups, respectively. A broad peak at 1.04 ppm, which disappears on addition of D$_2$O, is assigned to NH.

The ^{1}H NMR spectrum of a D$_2$O solution containing 1 and SiW$_{11}$Co is shown in Figure 1. Separate peaks are observed for the free ligand and the complex, indicating that the ligand exchange is slow on the NMR time scale. The signal originating from the complex consists of two strong
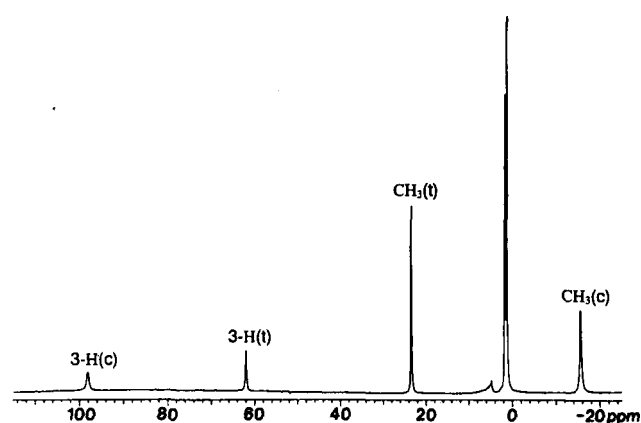

Figure 1. ^{1}H NMR spectrum of a D$_2$O solution containing 2,2-dimethylaziridine and SiW$_{11}$Co. The peaks from the complex are labeled.

peaks from the CH$_3$ groups and two weak peaks from the protons bonded to C$_3$. In each group there are one broad peak and one sharp peak. It has been shown that the NMR linewidths in a paramagnetic system are inversely proportional to the sixth power of the metal-nuclei distance.[11,12] The *cis* proton 3-H(c) and CH$_3$(c) with respect to the cobalt ion have shorter metal-nuclei distances than the corresponding *trans* proton 3-H(t) and CH$_3$(t). Therefore, the broad peaks at 98.0 and −15.6 ppm are assigned to 3-H(c) and CH$_3$(c), respectively, and the sharp peaks at 61.9 and 23.4 ppm to 3-H(t) and CH$_3$(t), respectively.

The ^{1}H NMR spectrum of a D$_2$O solution containing 1 and SiW$_{11}$Ni also exhibits two strong peaks and two weak peak originating from the complex (Figure 2). Comparing with the spectrum of the SiW$_{11}$Co complex, we can readily assign the peaks at 147, 64.0, 27.0, and −2.2 ppm to 3-H (c), 3-H(t), CH$_3$(t), and CH$_3$(c), respectively. A very broad signal at 140-50 ppm has not been identified. The isotropic shifts (= $\delta_{complex}$ - $\delta_{free\ ligand}$) of the SiW$_{11}$Co and SiW$_{11}$Ni complexes are listed in Table 1.

2-Methylaziridine. The ^{1}H NMR spectrum of 2 in CDCl$_3$ exhibits a multiplet at 1.956 ppm, and three doublets at 1.718 (J=5.5 Hz), 1.267 (3.5 Hz), and 1.168 ppm (5.4
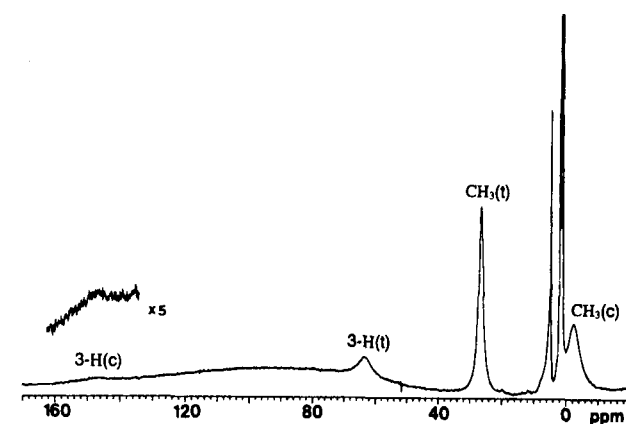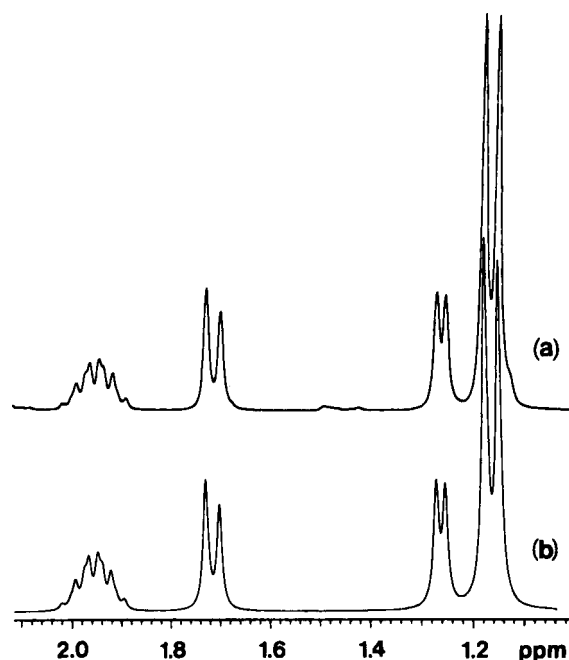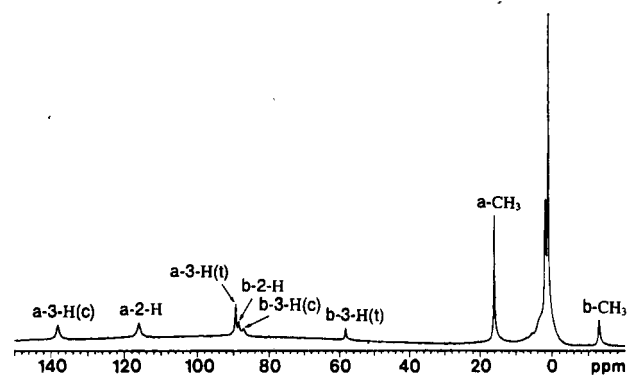

Figure 2. ^{1}H NMR spectrum of a D$_2$O solution containing 2,2-dimethylaziridine and SiW$_{11}$Ni. The peaks from the complex are labeled.

**Table 1.** Isotropic Shifts (in ppm) in Aziridine Derivatives Coordinated to $SiW_{11}Co$ and $SiW_{11}Ni$

Proton	$SiW_{11}Ni$	$SiW_{11}Co$	
	meas.	meas.	calc.
2,2-Dimethylaziridine			
3-H (*t*)	62.0	60.3	59.2
3-H (*c*)	145.0	96.4	96.0
CH₃ (*t*)	25.8	22.1	27.3
CH₃ (*c*)	−3.4	−16.9	−14.0
2-Methylaziridine (**2a**)			
3-H (*t*)	84.9	88.2	84.7
3-H (*c*)	144.4	136.2	134.4
2-H (*c*)	125.7	114.0	117.9
CH₃ (*t*)	15.5	15.0	18.8
2-Methylaziridine (**2b**)			
3-H (*t*)	63.2	56.2	60.2
3-H (*c*)	–	85.7	–
2-H (*t*)	94.0	86.5	82.9
CH₃ (*c*)	−2.4	−14.2	−10.1

Hz); see Figure 3a. The strong doublet at 1.168 ppm is assigned to the CH_3 group. The vicinal coupling constants for aziridine are $J_{cis}=6.3$ and $J_{trans}=3.8$ Hz, and the geminal coupling constant is very small.[13] The coupling constant between the methyl group and 2-H (5.2 Hz) is much larger than those between the methyl group and 3-H protons in propylene oxide.[14] Therefore, the multiplet may be assigned to 2-H, and the doublets at 1.718 and 1.267 ppm to 3-H$_t$ and 3-H$_c$, respectively, *t* and *c* representing *trans* and *cis* with respect to the CH_3 group. The order of the chemical

Figure 3. (a) Measured and (b) simulated ¹H NMR spectra of 2-methylaziridine in $CDCl_3$. See the text for the parameters used in simulation.

Figure 4. ¹H NMR spectrum of a D_2O solution containing 2-methylaziridine and $SiW_{11}Co$. The peaks from the complex are labeled.

shifts, $2\text{-}H > 3\text{-}H_t > 3\text{-}H_c > CH_3$, agrees with that observed for propylene oxide.[14] A simulated spectrum using the above chemical shifts and spin-spin coupling constants is shown in Figure 3b.[15]

The ¹H NMR spectrum of a D_2O solution containing **2** and $SiW_{11}Co$ exhibits two sets of peaks with different intensity (Figure 4). The chemical shift for the CH_3 group in the strong set is similar to that of $CH_3(t)$ and that for the weak set is similar to that of $CH_3(c)$ in **1**. Therefore, the strong set may be attributed to the linkage isomer with the CH_3 group *trans* to the cobalt ion (**2a**), and the weak set to the other isomer (**2b**). Most ¹H NMR peaks were assigned by saturation transfer technique. The two peaks at 88.5 and 87.0 ppm were assigned to 2-H(*t*) and 3-H(*c*) of the **2b** isomer, respectively, based on their intensities and line-widths. The assignments are shown in Figure 4.

Isomer **2a**   Isomer **2b**
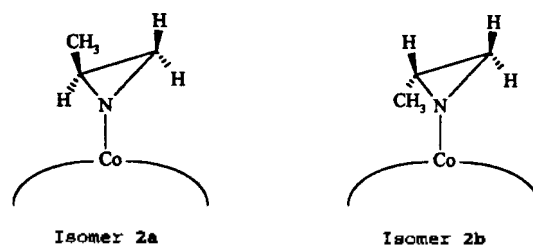
The ¹H NMR spectrum of a D_2O solution containing **2** and $SiW_{11}Ni$ also exhibit two sets of peaks with different intensity (Figure 5). Most of the peaks have been assigned on the assumption that the order of the chemical shifts in each set agrees with that of the $SiW_{11}Co$ complex. Changing the order worsens a quantitative analysis of the isotropic shifts (see below). It is not clear whether the peak at 96 ppm originates from 3-H(*c*) or 2-H(*t*) of the **2b** isomer. Assuming that the 3-H(*c*) peak of the **2b** isomer was too broad to be detected, we have tentatively assigned it to 2-H(*t*). The assignments are shown in Figure 5, and the isotropic shifts are given in Table 1.

Contact and Pseudocontact Shifts. The pseudocontact shift may be expressed as[5]

$$\delta_{dip} = \frac{\mu_0}{4\pi r^3} \times [\{\chi_{zz} - (\chi_{xx} + \chi_{yy})/2\} \times (3\cos^2\theta - 1)$$
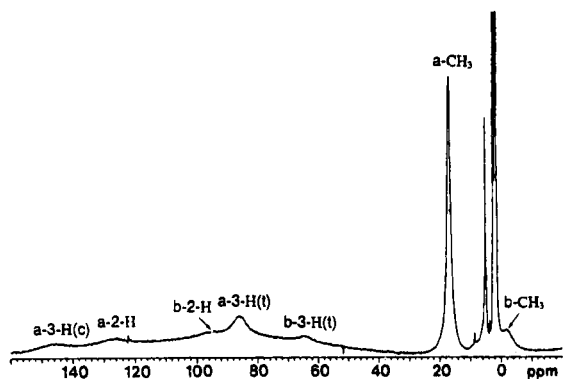$$+ (\chi_{xx} - \chi_{yy}) \times \sin\theta\cos 2\phi] \tag{2}$$

Figure 5. ¹H NMR spectrum of a D₂O solution containing 2-methylaziridine and SiW₁₁Ni. The peaks from the complex are labeled.

where χ_{xx} etc. are magnetic susceptibility components, and other symbols have their usual meaning. Since aziridines form only σ-bonds with transition metal ions, there is no π-bonding barrier that can prevent these ligands from rotating about the metal-nitrogen axis at room temperature. Then the second term due to the in-plane magnetic anisotropy can be neglected, and the pseudocontact shift is proportional to the geometric factor, $(3\cos^2\theta-1)/r^3$.

$$\delta_{dip} = \frac{\mu_0\{\chi_{zz} - (\chi_{xx} + \chi_{yy})/2\}}{4\pi} \times \frac{(3\cos^2\theta-1)}{r^3} \tag{3}$$

For an octahedral nickel(II) complex, which has an orbitally non-degenerate $^3A_{2g}$ ground state with excited states far removed in energy, the orbital contribution is small and so is the magnetic anisotropy.[5] So the pseudocontact shifts have been neglected in interpretation of isotropic shifts for most nickel complexes.[16,17] If the isotropic shifts originate only from the contact shifts, the ratio of the isotropic shifts for various protons in a given ligand should be independent of the nickel complex to which the ligand is coordinated.

It is of interest to compare the data for our nickel complexes with those of bis(2,4-pentanedionato)nickel(II) {Ni (acac)₂} complexes.[7] Since the exchange rates of aziridines coordinated to Ni(acac)₂ are fast, only relative isotropic values were determined. The ratio of isotropic shifts for H(*t*) and H(*c*) in N-alkylaziridine coordinated to Ni(acac)₂ is 0.58 : 1.0,[7] while it is 84.9 : 144.4 (0.59 : 1.0) for **2a** coordinated to SiW₁₁Ni. The agreement is excellent. The ratio of isotropic shifts for CH₃(*t*) and CH₃(*c*) in **1** coordinated to Ni(acac)₂ is 6.41 : -1.00, while it is 25.8 : -3.4 (7.6 : -1.0) for **1** coordinated to SiW₁₁Ni. Here the agreement is not so excellent, indicating that the contact shifts are dominant but the pseudocontact shifts cannot be neglected in SiW₁₁Ni complexes.

Now we consider the isotropic shifts in the cobalt complexes. Since both Co^{2+} and Ni^{2+} ions in distorted octahedral environments have two σ electrons in the d_{z^2} and $d_{x^2-y^2}$ orbitals, contact shifts due to σ-electron delocalization in the SiW₁₁Co complex may be assumed to be proportional to the corresponding contact shifts for the SiW₁₁Ni complex.

Now Eq. (1) may be expressed as

$$\delta_{iso}(Co) = C_1 \times \delta_{con}(Ni) + C_2' \times \frac{(3\cos^2\theta-1)}{r^3} \tag{4}$$

where C_1 and C_2' are proportionality constants. The iso-

tropic shifts in the nickel complexes can be expressed in a similar manner.

$$\delta_{iso}(Ni) = \delta_{con}(Ni) + D_2 \times \frac{(3\cos^2\theta-1)}{r^3} \tag{5}$$

If geometric factors are assumed to be the same for the cobalt and nickel complexes, the following equation is obtained.

$$\delta_{iso}(Co) = C_1 \times \delta_{iso}(Ni) + C_2 \times \frac{(3\cos^2\theta-1)}{r^3} \tag{6}$$

where C_2 is $(C_2'-C_1D_2)$. The geometric factors have been calculated using the bond lengths and angles of aziridine[18] and a Co-N length of 2.16 Å.[19] The resulting values are 0.0250 for H(*t*), 0.0182 for H(*c*), 0.0129 for CH₃(*t*), and -0.0116 Å⁻³ for CH₃(*c*). The values for the methyl groups, which rotate fast about the C-C axis, are average values for all directions. The two unknown constants, C_1 and C_2, can be determined from measured δ_{iso} values for two protons. However, different values of C_1 and C_2 are obtained for different combinations of the protons. We have chosen C_1 and C_2 values which produce the least mean square difference between the measured and calculated δ_{iso} values. The resulting values are C_1=0.530 and C_2=1055 for **1**, C_1=0.881 and C_2=396 for **2a**, and C_1=0.688 and C_2=728 for **2b**.[20] Calculated δ_{iso} values using these constants (Table 1) agree reasonably with the measured values.

It is of interest to note that values of C_2 are positive. Since D_2 is much smaller than C_2', and C_1 is less than 1, C_2 is close to C_2' which is proportional to $(\chi_\parallel-\chi_\perp)$. Thus $(\chi_\parallel-\chi_\perp)$ is positive for all three aziridine complexes. The corresponding values for pyridine derivatives were found to be negative.[17] Since the geometric factor for CH₃(*c*) is negative, the large upfield shift for this group in the SiW₁₁Co complexes as compared with the SiW₁₁Ni complexes can be explained only when C_2 is positive. (Negative pseudocontact shifts correspond to upfield shifts.)

It was shown that the pseudocontact shifts in the SiW₁₁-Co complexes of pyridine derivatives were sensitive to the ligand basicity.[17] The d orbitals have the ordering d_{xz}, d_{yz} $<d_{xy}<d_{z^2}<d_{x^2-y^2}$ for these complexes. The energy difference between the $d_{x^2-y^2}$ and d_{z^2} orbitals, or that between the d_{xy} and d_{xz}, d_{yz} orbitals may be used as a measure of deviation from the octahedral field and hence the magnetic anisotropy. As the ligand basicity increases, the d_{xz}, d_{yz} orbitals are destabilized, reducing the energy difference and hence the magnetic anisotropy. If the ligand is very basic, the d orbital ordering may be reversed to $d_{xy}<d_{xz}$,d_{yz} and $(\chi_\parallel-\chi_\perp)$ may become positive. Aziridines are quite basic, but the pK_a value of the conjugate acid of aziridine, 8.04, is not so large as that of 4-aminopyridine (pK_a=9.11),[21] the SiW₁₁Co complex of which has $(\chi_\parallel-\chi_\perp)$ <0. So other factors may be involved in determining the sign of $(\chi_\parallel-\chi_\perp)$. It has been argued that the energies of the π bonding and antibonding orbitals of the ligand are more important than the σ-type interactions between the metal and the axial ligands in determining the energies of the d_π orbitals for low-spin ferric porphyrins with axial pyridine-type ligands.[22] So the sign of $(\chi_\parallel-\chi_\perp)$ for aziridines may not be predicted by simple comparison of pK_a values of aziridines with those of pyridine-type ligands. More work is needed to better explain the positive

sign of $(\chi_{\parallel} - \chi_{\perp})$ for aziridines.

In summary, values of $(\chi_{\parallel} - \chi_{\perp})$ for the $SiW_{11}Co$ complexes of aziridine derivatives have been found to be positive by analysis of the isotropic NMR shifts, while that for the $SiW_{11}Co$ complexes of pyridine derivatives is negative. This result indicates that the ordering of d_{xy} and d_{x^2}, d_{yz} orbitals in $SiW_{11}Co$ complexes can be reversed by ligands.

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Analysis of Complex Forced Rayleigh Scattering Decay Profiles for the Diffusion of Methyl Yellow in Binary Solution

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The nature and analysis methods of complicated decay profiles found in forced Rayleigh scattering (FRS) have been investigated for the probe diffusion of methyl yellow in 2-propanol. The complementary shifted and ground state grating effect, which is known to be the origin of non-single exponential decays, was analyzed by non-linear regression fitting to a double exponential model function. We confirmed that the parameters were highly correlated so that it was difficult to extract a unique set of parameters in the presence of experimental noise. Nevertheless, a reasonable range of decay time constants could be estimated from the grating spacing dependence.

Introduction

Recently the forced Rayleigh scattering (FRS) technique has been widely used for the study of mass diffusion in various media.[1-10] The technique measures the decay of the light intensity diffracted from a periodic concentration grating created by the illumination of an optical fringe pattern within a sample containing an appropriate photoprobe. In order for the concentration grating to diffract light, the photo-reaction product (shifted state) must possess different optical properties from the unshifted state either in absorptivity (amplitude grating) or in refractive index (phase grating), or both.[11-14] If the transient sinusoidal concentration profile decays with a single relaxation time constant, the diffracted

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