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A spectrophotometric method for the quantification of outer-sphere coordination: A bicyclic ammonium cation with the hexacyanocobaltate(III) anion

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The outer-sphere interaction between the $Co(CN)_6^{3-}$ anion with the two protonated forms of DABCO (1,4-diazabicyclo[2.2.2]octane) was investigated by a spectrophotometric titration method. The resulting outer-sphere stability constant for the diprotonated $DABCOH_2^{2+}$ cation was determined as $\log K_{OS} = 2.53 \pm 0.01$, compared to the value of 2.77 ± 0.12 obtained using conventional potentiometric titration results. Absorption changes were very small; however, good reproducible results were obtained for the higher charged diprotonated cation interaction and the method may have general application.

INTRODUCTION

Recently there has been considerable interest in outer-sphere (or second sphere) coordination. The number of host-guest supramolecular complexes involving non-covalent interactions has rapidly expanded since the initial work of Lehn and coworkers.[1] The interactions are largely electrostatic in nature; however, hydrogen bond formation may also play a role in determining the stability of the supercomplexed species.

Anion receptor molecules are important in many areas of chemistry and biochemistry. An understanding of the stability of these complexes is essential for determining their potential applications in such areas as phase transfer, membrane sensors[2,3] and nucleotide transport.[3,4] Numerous studies involving cyclodextrins and calixarenes have also been documented.[5-10] Polyammonium macrocycles have been widely used as anion receptors as they can form adducts with both organic and inorganic anions.[11-15] Macrobicyclic and macrotricyclic ammonium ions have also been investigated as anion receptors.[16-20]

Bianchi *et al.*[21] have recently reviewed a range of stability constants for anion coordination. Potentiometric titration methods are the most frequently employed. In comparison, there are only a very limited number of examples of spectrophotometric determination in the literature.[17,18,22] Potentiometry is well suited if the outer-sphere complexation reaction is coupled to a protonation equilibrium in an accessible pH region, i.e. pK_a values between 3 and 11 for accurate determinations.

$$CatH^+ + An^- \overset{K_{OS}}{\rightleftharpoons} [CatH^+ - An^-]$$

$$CatH^+ \overset{pK_a}{\rightleftharpoons} Cat + H^+$$

Many of the cationic receptors are ammonium and polyammonium ions with pK_a values in the optimal pH region and the investigation of their interaction with anions can be done by potentiometric titrations. It is interesting to note that the ability to form hydrogen bridges is restricted to weakly acidic protons, coinciding with the requirement for pH titrations.

Spectrophotometric titrations are alternative methods with a range of advantages: (a) the outer-sphere interaction needs not to be coupled to a deprotonation equilibrium, (b) investigations at high and low pH are possible, (c) no restriction to aqueous solution applies, and (d) structural information about the adducts may be gained from the absorption spectra of the adducts.

The most important requirement of the spectrophotometric method is that measurable spectral changes must be observed.[23,24] However, when outer-sphere interactions that do not involve charge

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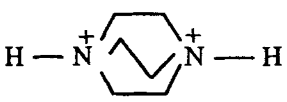
transfer are examined the spectral changes are very small, resulting only from a change in the solvation shell. These very small absorbance changes have limited the use of spectrophotometric methods for determining outer-sphere coordination.

In this contribution we report on the spectrophotometric determination of the outer-sphere interaction between the $Co(CN)_6^{3-}$ anion with the two protonated forms of DABCO (1,4-diazabicyclo[2.2.2]-octane). Titrations were performed at pH 2 and pH 7.5, resulting in values for outer-sphere stability constants, K_{OS}, for the diprotonated $DABCOH_2^{2+}$ (**1**) and the monoprotonated $DABCOH^+$ cations. Absorption changes were very small, yet good reproducible results were achievable for the stronger interaction. The results were confirmed with potentiometric pH titrations.



(1)

RESULTS

The deprotonation constants of $DABCOH_2^{2+}$, as determined potentiometrically at 25 °C and 0.1 M ionic strength, are $pK_{a1} = 8.79$ (± 0.01) and $pK_{a2} = 3.02$ (± 0.02). The values compare well with those determined by Paoletti *et al.*[25] as $pK_{a1} = 8.82$ (± 0.01) and $pK_{a2} = 2.97$ (± 0.02) at 25 °C and 0.1 M ionic strength.

In order to investigate the interaction between the diprotonated and monoprotonated DABCO and $Co(CN)_6^{3-}$, spectrophotometric titrations were performed at pH 2 and 7.5. Figure 1 shows the spectral changes observed at 380 nm for the titration of 2 ml of 0.0025 M $Co(CN)_6^{3-}$ with 0.05 mL of 0.1 M $DABCOH_2^{2+}$ in (a) and with $DABCOH^+$ in (b). The data displayed are not corrected for dilution. In Fig 1(a), an increase of absorption at low pH is obvious and straightforwardly ascribed to the formation of an adduct with higher molar absorptivity than the initial hexacyanocobaltate. At pH 7.5 the change in absorption is mainly due to dilution.

Analysis of the titrations, which are measured at many wavelengths between 400 and 300 nm, yielded equilibrium constants and absorption spectra of the adducts. The equilibrium constants are displayed in Table 1.

a) $Co(CN)_6^{3-}$ – $DABCOH_2^{2+}$

The equilibrium constants for the interaction with the doubly protonated cation are fairly large and well defined as indicated by the consistency of the results for repeated experiments. The values are also similar to the ones determined potentiometrically.

Figure 2 shows the calculated concentration profiles for the spectrophotometric titrations. Only a fraction of the anions and cations are actually interacting under the conditions chosen for the titration. Due to precipitation, presumably of the salt, it was impossible to work with higher concentrations or to add a substantial excess of ligand.

The absorption spectra for the adduct is displayed in Fig 3, together with the spectrum of $Co(CN)_6^{3-}$. The observed spectral changes were very small upon formation of the outer-sphere complex. This is expected, since the formation of the complex only effects the solvation shell or outer coordination sphere. The spectrum of the hexacyanocobaltate(III) anion, $Co(CN)_6^{3-}$, exhibits two Laporte forbidden *d-d* bands at 313 and 260 nm corresponding to the $^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1A_{1g} \rightarrow {}^1T_{2g}$ electronic transitions respectively.[26] For a transition metal complex the wavelength of the absorption depends on the separation (splitting) of the *d* states. For $Co(CN)_6^{3-}$, this splitting is a function of the polarization of the Co(III) cation by the CN^- ligands and depends on the separation distance of the ligand and the cation. Ion-pair formation will be expected then to have very little effect on this *d-d* splitting because of the large separation between the complex anion and ligand as ion-pairs.[27]

Figure 3 also shows the slight increase in absorbance that occurs upon complex formation. This can be explained in terms of the relaxation of the Laporte selection rule. Outer-sphere complex formation removes the centre of symmetry that is present in the octahedral $Co(CN)_6^{3-}$ ion alone. The octahedral geometry of the anion is then effectively distorted and this provides a pathway for some absorption intensity.[28]

b) $Co(CN)_6^{3-}$ – $DABCOH^+$

The interaction between the monoprotonated cation and the hexacyanocobaltate is much weaker. For this reason, under the experimental conditions in the spectrophotometric and the potentiometric titrations, there is very little adduct formation. The numerical fitting of the measurements then yields equilibrium constants which are very poorly defined as indicated by the wide variation for repeated experiments. From the results an equilibrium constants of around $10^{0.5 \pm 0.5}$ can be estimated. The absorption spectrum of the adduct is basically not defined as very little is actually formed.

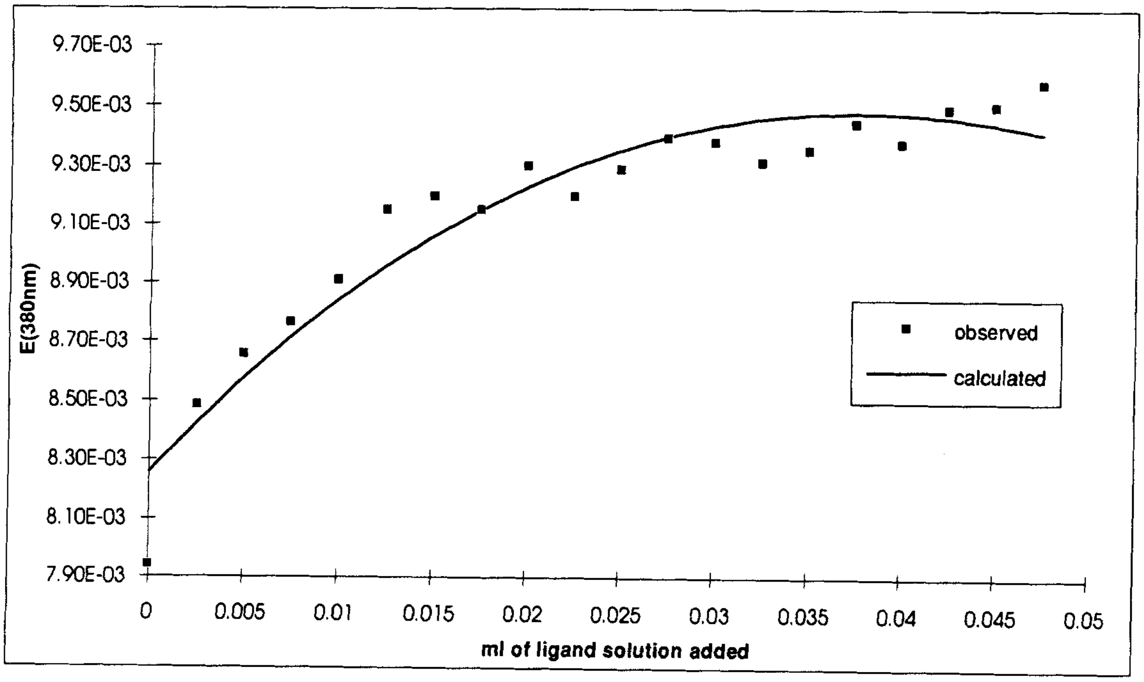


Figure 1(a) Spectral changes at 380 nm for the titration of $Co(CN)_6^{3-}$ with $DABCOH_2^{2+}$.

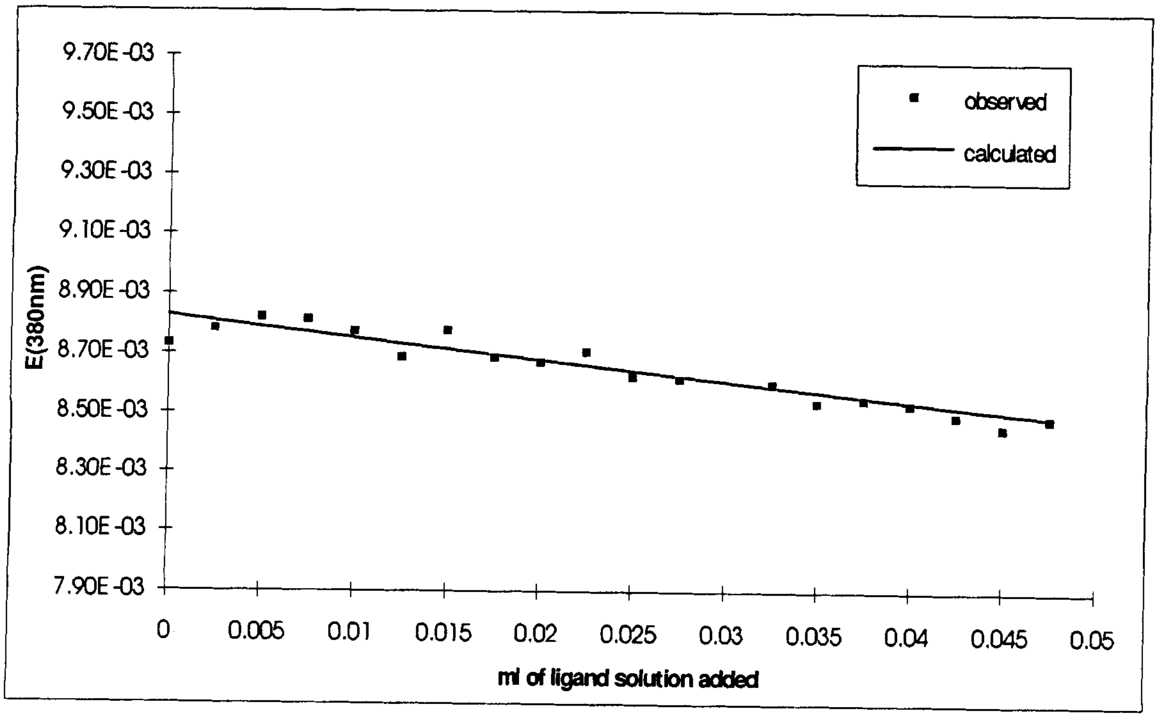
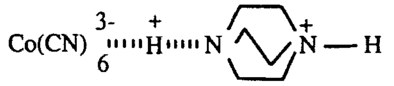


Figure 1(b) Spectral changes at 380 nm for the titration of $Co(CN)_6^{3-}$ with $DABCOH^+$.

DISCUSSION

Two effects contribute to the outer-sphere interaction between ammonium ions and anions: electrostatic attraction and hydrogen bridge formation. An indication about the relative importance of these contributions can be gained from our results. Under our experimental conditions only 1:1 complexes were observed. Because of the spherical geometry of the anion and the linear-like geometry of the cation, only a monodentate interaction is possible (**2**)



(2)

with formation of one single hydrogen bond irrespective of whether $DABCOH_2^{2+}$ or $DABCOH^+$ is interacting. The contribution of the hydrogen bridge to the overall stability is probably similar in both cases. The substantial difference between the stabilities for the differently protonated forms of DABCO, therefore, has to be attributed to the difference in the charge. Thus, the main contribution is the electrostatic interaction. Both the Bjerrum and Fuoss theories also predict that the stabilities of ion-pairs are greater for species of higher charge.[29]

Table 1 Stability constants determined by spectrophotometric and potentiometric methods at 25 °C and 0.1 M ionic strength

$DABCOH_2^{2+} + Co(CN)_6^{3-}$ Log K_{OS}		$DABCOH^+ + Co(CN)_6^{3-}$ Log K_{OS}	
Spec	*Pot*	*Spec*	*Pot*
2.52	2.88	3.39	−0.34
2.54	2.77	1.77	0.58
2.54	2.65	−0.38	0.93

The weak Lewis basicity of the hexacyano complex might be the reason for the weak hydrogen bridge. Interaction of ammonium ions with stronger Lewis bases is expected to be enhanced by hydrogen bonding.

In this investigation we tested the feasibility of spectrophotometric titrations as a technique to quantify outer-sphere interaction. The method relies on spectral changes which are expected to be small. To examine the method we chose a reaction between a cation and anion pair for which (a) spectral changes were expected to be small and (b) the results could be tested with the established method of potentiometric pH titrations. The results are encouraging and in spite of the small spectral changes the equilibrium constants determined spectrophotometrically are identical with the potentiometric values. The very small absorbance changes involved with the complexation of a transition metal complex and cyclodextrins have also been documented but not quantified.[9] It is worthwhile noting here that outer-sphere interaction is often not easily quantified, and different methods can result in significantly different results.[30]

Spectrophotometric titrations can be applied to investigate cations such as polyalkylammonium ions

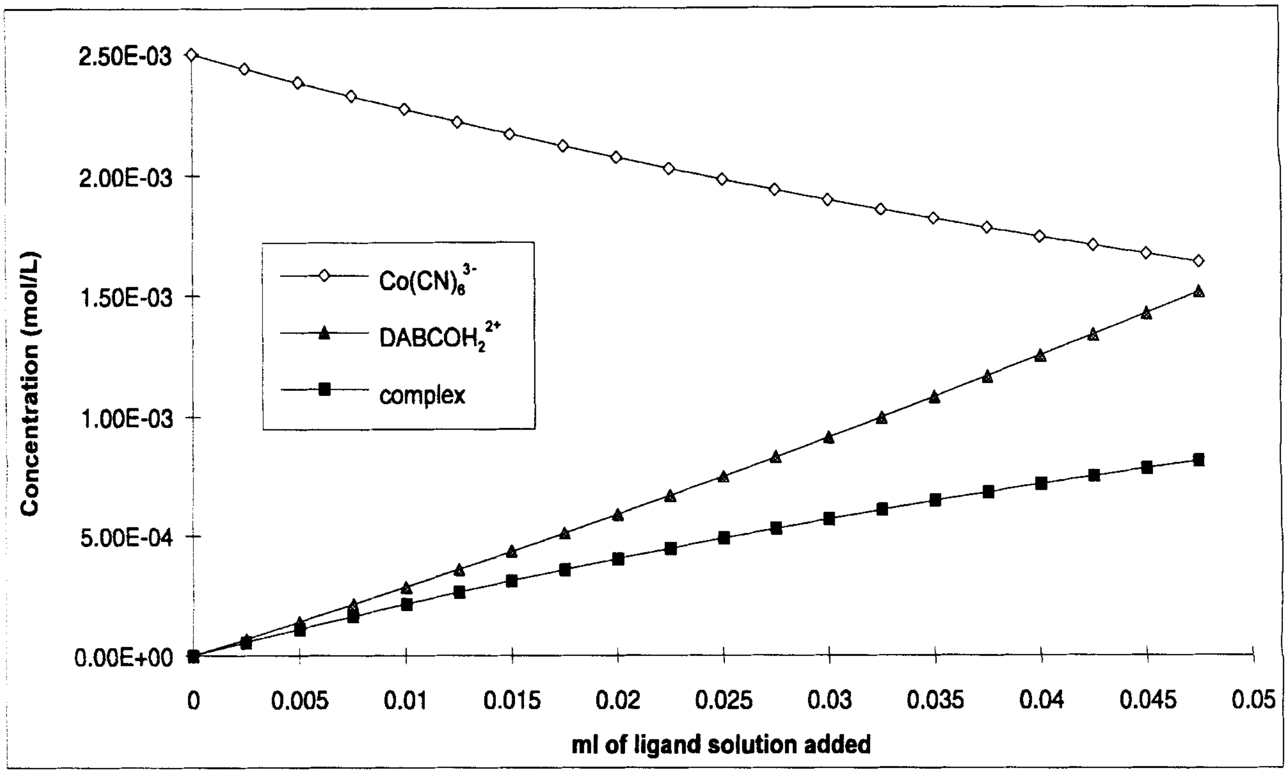


Figure 2 Concentration profiles for spectrophotometric titration of $Co(CN)_6^{3-}$ with $DABCOH_2^{2+}$.

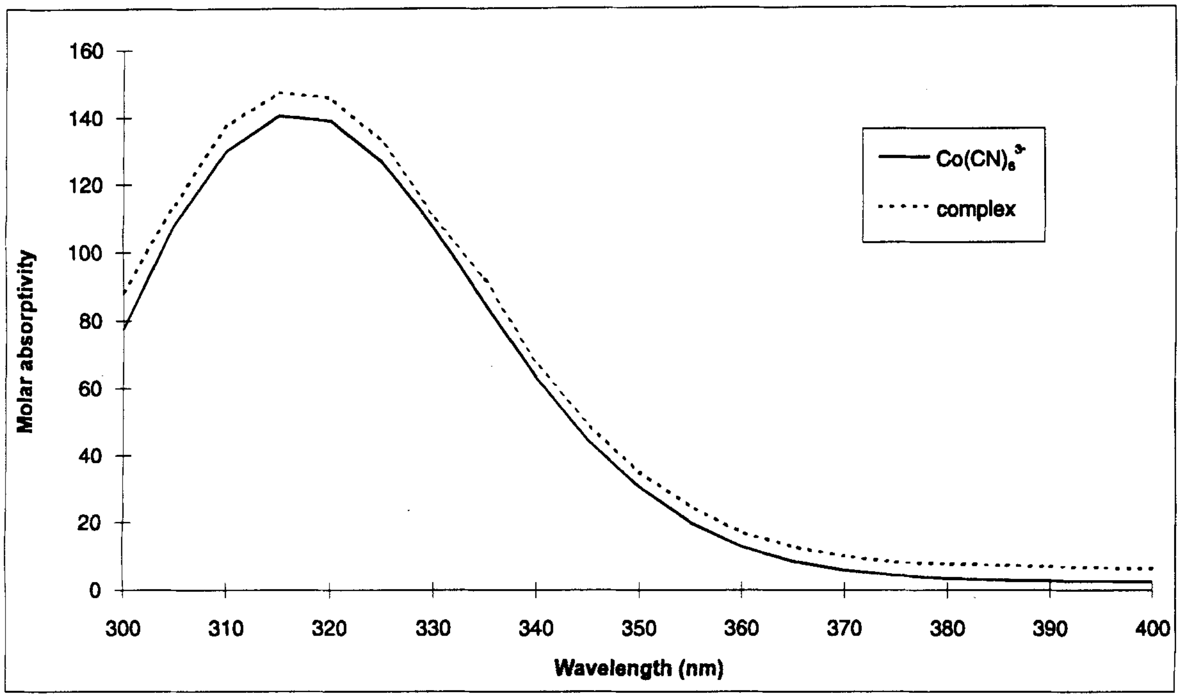


Figure 3 Molar absorptivity of $Co(CN)_6^{3-}$ and calculated molar absorptivity for the outer-sphere complex.

which cannot be investigated potentiometrically. Further, spectral changes are expected to be significantly larger if charge-transfer bands are influenced by outer-sphere interaction.

EXPERIMENTAL

Synthesis: N,N′-dihydro-1,4-diazabicyclo[2.2.2]octanium dichloride (1)

1,4-diazabicyclo[2.2.2]octane (DABCO) (10.0 g, 0.089 mol) was dissolved in water (200 mL) and concentrated hydrochloric acid was carefully added until the pH ≈ 2. The solution was then taken to dryness and the resulting white solid was recrystallized from methanol affording the product (**1**). ^{1}H n.m.r. (δ D_2O) 3.76 ppm. (pH ≈ 2.5). The spectra were recorded on a Jeol FX90Q spectrometer. A downfield shift is observed compared to the unprotonated DABCO (2.74 ppm) due to the deshielding effect of the quaternary nitrogen.

Spectrophotometric titrations

Absorption spectra were recorded on a Hitachi 220A instrument controlled by an IBM-compatible PC. An automated stepper-motor driven syringe, stirrer and pH electrode were also controlled by the computer. The cell compartment was thermostatted to 25 °C. The titrations were performed in the 1 cm absorption cell in a set-up similar to the one reported by Schmidtchen.[17] Data analysis was carried out using the program SPECFIT.[31]

In a typical experiment 20 increments of 0.0025 mL of 0.1 M (**1**) were added to 2.0 mL of the hexacyanocobaltate(III) solution (0.0025 M), i.e. a 1:1 molar ratio. Both solutions were adjusted to pH 2.0 with HCl. The pH of the solution was measured and did not change during the titration. Identical titrations with the monoprotonated cation were performed with the pH adjusted to 7.5. All solutions were filtered and the ionic strength was kept constant at 0.1 M with tetraethylammonium perchlorate (TEAP). The absorption was measured between 400 and 300 nm at 5 nm intervals. The concentrations and increments were chosen to avoid precipitation which occurred at higher concentrations. Titrations were repeated at least 3 times.

Potentiometric titrations

Titrations were obtained with a Metrohn 665 dosimat burette controlled by an IBM-compatible PC. Experiments were carried out at 25 °C in aqueous solution of constant ionic strength (0.1 M TEAP) under nitrogen. NBS buffers of pH 4 and 7 were used to calibrate the potentiometer. The program TITFIT[32] was used for analysis of the data. Stability constants were obtained by iterative refinement.

To determine the deprotonation constants of

$DABCOH_2^{2+}$ an initial titration was performed on (**1**) alone. 65 × 0.002 mL increments of 0.4 M NaOH were added to 25 mL of a 6.0×10^{-4} M solution of (**1**). An 3.2×10^{-4} M acid excess was also added. In order to investigate the outer-sphere interaction, $DABCOH_2^{2+}$ and $DABCOH^{+}$ were titrated in the presence of a 5 fold excess of $Co(CN)_6^{3-}$. Typically, 65 × 0.002 mL increments of 0.4 M NaOH were added to 25 mL of a 6.0×10^{-4} M solution of (**1**) and 2.5 mL of 0.03 M $Co(CN)_6^{3-}$. The total concentrations were 6.0×10^{-4} M and 3.0×10^{-3} M for (**1**) and $Co(CN)_6^{3-}$, respectively. Titrations were repeated at least 3 times.

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