On the assumption that inductive effects are negligible, the effect of increasing alkyl substitution on the attacking atom in the entering nucleophile may be calculated by using the Taft steric parameter[40] E_s (see Table III), defined as $E_s = \log (k/k_0)$, where k_0 is a reference rate constant for the least sterically hindered member of the series (MeOH, $k_0 = 2.92$ s^{-1}). In coordination chemistry, this approach has been used by Rorabacher and co-workers[41] to measure steric effects of alkyl substituted mono- and diamines reacting with Ni(II) and more recently by Jones et al.[42] in the kinetics of the square-planar complex $[Pd(dien)OH_2]^+$ (dien = diethylentriamine) with an extended series of dialkyl sulfides. A rough straight line can be obtained on plotting the values of E_s in Table III against that reported by Jones (slope = 0.37, r = 0.969). While it seems clear that steric crowding produced during the formation of a five-coordinate transition state by two alkyl groups in the thioethers R_2S exceeds that produced by the only one in ROH, a good deal more data for other systems are required to test thoroughly the validity of such comparisons.

Nucleophile-Dependent Pathway. A definite second-order contribution k_2 (M^{-1} s^{-1}) arises from the direct displacement of Cl^- from *cis*-$[Pt(PEt_3)_2(m\text{-}MeC_6H_4)Cl]$ by the strong nucleophile thiourea. This reagent is known to possess good π-acceptor properties and to stabilize the 5-coordinate transition state in reactions with Pt(II) substrates via electron delocalization. This capacity is usually enhanced by strong σ donation of the coordinated ligands to the metal atom in the ground state.[12] The intimate mechanism of the reaction can be described as a two-step addition-elimination process, in which the rate-determining step is the formation of a 5-coordinate transition state having both the incoming and the leaving group firmly bonded to the metal, followed by a rapid conversion into the square-planar product. A clear example of this pattern of behavior can be found in a study of solvent effects on the halide displacement by thiourea from the complexes *trans*-$[Pt(PEt_3)_2(R)X]$ (R = CH_3, C_6H_5, m-FC_6H_4; X = Cl, Br, I, N_3, NO_2).[43] The ease of replacement of Br^-, N_3^-, and NO_2^- relative to chloride, assumed as reference, was found to be essentially the same in methanol and dimethyl sulfoxide, suggesting a small degree of Pt-X bond breaking in the transition state which makes solvation of the leaving group kinetically unimportant.

Accordingly, we observe that the solvent effect in the reactions with thiourea (see Table I) is very small compared to that found in the isomerization and it goes in the opposite direction, confirming that the Pt-Cl bond remains essentially intact during the formation of the 5-coordinate transition state.

Although HDB interactions of the protic solvents with nitrogens of the reagent $SC(NH_2)_2$ could account for the trend observed in the reactivity along the examined series, a discussion of these small effects at this stage risks being only speculative in nature. A fuller understanding of the problem could involve measures of volumes of activation[44] or dissection of the solvent effects into initial-state and transition-state components, by the use of appropriate thermodynamic parameters for the reactants. An analysis of this type has been performed successfully by Burgess and co-workers, who studied the kinetics of the reaction of 2,2'-bipyridyldichloroplatinum(II)[45a] and of *cis*-dichlorobis(4-cyanopyridine)platinum(II)[45b] with thiourea in binary aqueous solvent mixtures, showing that the solvation of the initial complex is the most important factor controlling reaction rates.

Acknowledgment. The authors gratefully acknowledge the financial assistance of the Ministry of Education and of the Italian CNR.

Registry No. *cis*-$[Pt(PEt_3)_2(m\text{-}MeC_6H_4)Cl]$, 70445-93-1; *trans*-$[Pt(PEt_3)_2(m\text{-}MeC_6H_4)Cl]$, 74824-29-6; I^-, 20461-54-5; $SC(NH_2)_2$, 62-56-6.

Supplementary Material Available: Listings of observed rate constants for isomerization of *cis*-$[Pt(PEt_3)_2(m\text{-}MeC_6H_4)Cl]$ and chloride displacement by I^- and $SC(NH_2)_2$ (5 pages). Ordering information is given on any current masthead page.

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Formation of Polynuclear Cupric Halides in Cationic Reversed Micelles

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Received March 26, 1980

The structure of cupric chloride and bromide complexes cosolubilized in cationic reversed micelles has been investigated by means of electronic absorption and electron paramagnetic resonance spectroscopy. At low water concentrations (0.3 M or less), the principal amount of water is bound to surfactants and does not go into solvation equilibrium with the copper. Under the circumstances, cupric chloride cosolubilized in the micelles showed absorption bands at 408 and ~1150 nm, and it was EPR negative. The structure has been elucidated as a distorted-tetrahedral configuration of polymeric form. It converts to a monomeric distorted tetrahedron with the increase in water concentration, leading eventually to a distorted octahedron normally observable in an aqueous medium. Cupric bromide behaved in a similar manner. The origin of these unique solution structures of cupric halides is discussed in conjunction with the microenvironment surrounding the cupric ion in a restricted field provided by cationic reversed micelles.

Introduction

Reversed micelles, aggregates between surfactants and polar solutes formed in apolar media, certainly provide a specific and restricted field.[2,3] Depending on the concentrations of surfactant and water, the tightness of surfactant-water interaction,[4] the size of water pool, and the microscopic viscosity[5] and polarity[6] of the interior can be varied. During the past decade, information about the unique feature of reversed micelles on organic reactions has been accumulated.[2,3] However, one has scarcely paid attention to the state and nature of solutes being cosolubilized in reversed micelles in conjunction with the coordination chemistry, especially under very limited conditions where the molar ratio of water to surfactant is about unity.[7,8] Very recently, J.S. and T.H. found that the configurational change between tetrahedral and octahedral species of cobalt(II) complexes takes place in several reversed micelles.[7] The phenomenon was interpreted in terms of solvochromism and thermochromism which were accompanied by the elimination–addition equilibrium of water between the metal ion and the surfactant. Moreover, it seemed to be certainly connected with the rigidity of the aggregates between surfactant and water. Extending our studies on the coordination chemistry in reversed micelles, in this work we have explored the structure of copper(II) complexes in cationic reversed micelles as a model of a metalloenzyme pocket.[9]

The structure of chlorocuprates(II) in solutions as well as in crystals has attracted much attention of inorganic chemists, and numerous studies have been performed in the past.[10] According to the crystallographic studies on Cs_2CuCl_4, the complex takes a distorted-tetrahedral configuration.[11] On the other hand, the existence of tetragonally distorted octahedral chlorocuprates of polymeric nature has also been demonstrated for crystals of $(NH_4)_2CuCl_4$, $(CH_3NH_3)_2CuCl_4$, and $(C_2H_5NH_3)_2CuCl_4$.[12] The crystalline $Cu_2Cl_4(CH_3CN)_2$ and $Cu_5Cl_{10}(C_3H_7OH)$ both also show a virtually planar structure.[13] Besides, monomeric and dimeric trigonal-bipyramidal geometries have been found for $Cr(NH_3)_6CuCl_5$[14] and $Co(en)_3CuCl_5(H_2O)$,[15] respectively. A relationship between the electronic spectra and structure of these complexes has also been discussed very extensively.[16–19] The most likely structure of chlorocuprate ions in aqueous media was considered to be either the distorted-tetrahedral (D_{2d} symmetry) or the square-planar geometry (D_{4h} symmetry).[20,21] Helmholz and Kruh favor the former configuration,[11] while Eswein et al. take the latter one for the same complex.[22] Quantum-chemical calculations suggest that a flattened tetrahedron D_{2d} is preferred over D_{4h} and T_d for $CuCl_4^{2-}$.[23] It is, however, uncertain whether the conclusion is true for the solution structure or not. In addition to these mononuclear complexes, polynuclear chlorocuprates may be formed under certain circumstances even in solution[24] just as in the solid state.[12]

Totally different from these previous findings, electronic absorption and electron paramagnetic resonance spectroscopic studies on the copper(II) halide complexes in cationic reversed micelles suggested to us that the structure of the complex in the micelles containing only a limited amount of water is a halogen-bridged polynucleus of copper(II) of D_{2d} symmetry. Depending on the water concentration and temperature, solvochromic and thermochromic transformations of the complex were observed.

Experimental Section

Materials. $CuCl_2 \cdot 2H_2O$ and $CuBr_2$ are commercially available as analytical grade reagents. Commercial chloroform was purified as follows: Following removal of ethanol it was dried over phosphorus pentoxide, distilled, and stored over Linde 4A molecular sieves in a brown container. Hexadecyltrimethylammonium bromide (CTABr) was obtained from Wako Pure Chemical Industries and recrystallized from acetonitrile. Hexadecyltrimethylammonium chloride (CTACl) was prepared by passing CTABr through an Amberlite IRA 400 column (chloride form) with methanol as an eluant. Dimethyldioctadecylammonium bromide (QDBr) and chloride (QDCl) were prepared by the reaction of dimethyloctadecylamine with the corresponding octadecyl halide. Anal. Calcd for $C_{38}H_{80}NBr \cdot 0.5H_2O$: C, 71.32; H, 12.76; N, 2.19. Found: C, 71.65; H, 12.30; N, 2.13 (mp for QDBr 164–165 °C). Calcd for $C_{38}H_{80}NCl \cdot H_2O$: C, 75.50; H, 13.34; N, 2.32. Found: C, 75.47; H, 13.77; N, 2.26 (mp for QDCl 152–153 °C).

Miscellaneous Measurements. For spectroscopic measurements, a given amount of detergent was dissolved in chloroform. The resulting solution (usually 10 mL) was delivered to a reference and sample cuvette (3 mL each). After thermal equilibrium was attained at 25.0 °C, 0.20 μL of 3.8 M aqueous cupric halide solution was injected with a microsyringe to the sample cell, which was then shaken thoroughly on a Vortex mixer. An appropriate amount of water was progressively added in a similar manner, and spectra were taken each time. Electronic absorption spectra and near-infrared spectra were determined on a Hitachi 323 recording spectrophotometer. Electron paramagnetic resonance spectra were recorded on a JEOL JES-ME-3X X-band spectrometer with 100-kHz field modulation at 60 to −20 °C. The magnetic field was calibrated with Mn(II)/ZnO standard sample. The amount of water in a solvent or solution was determined by a Karl Fischer automatic titration apparatus, Model MK-A, of Kyoto Electronics Co.[7,9] The apparent freezing point of water solubilized in reversed micelles was determined by nuclear magnetic resonance technique on a JEOL MH-100 spectrometer.

Results

Electronic Spectra. In aqueous solution, the copper(II) ion is octahedrally hydrated to afford blue $[Cu(H_2O)_6]^{2+}$. When a concentrated aqueous solution of cupric bromide is cosolubilized in the CTABr/chloroform reversed micelles, it gives an intense brown color. Similarly, cupric chloride in the CTACl/chloroform micelles gives a yellow solution. These colors are sensitive to the amount of water present in the system. The brown or yellow color gradually fades with the increase in water concentration, and finally the solution becomes violet or blue, respectively. This state of affairs is shown in the visible spectra of cupric halides determined over a wide range of water concentration (Figure 1). At the lowest water concentration (0.047 M) accessible in the 0.20 M CTABr/chloroform system, cupric bromide shows three absorption maxima at 284, 380, and 470 nm. At first, only the intensity

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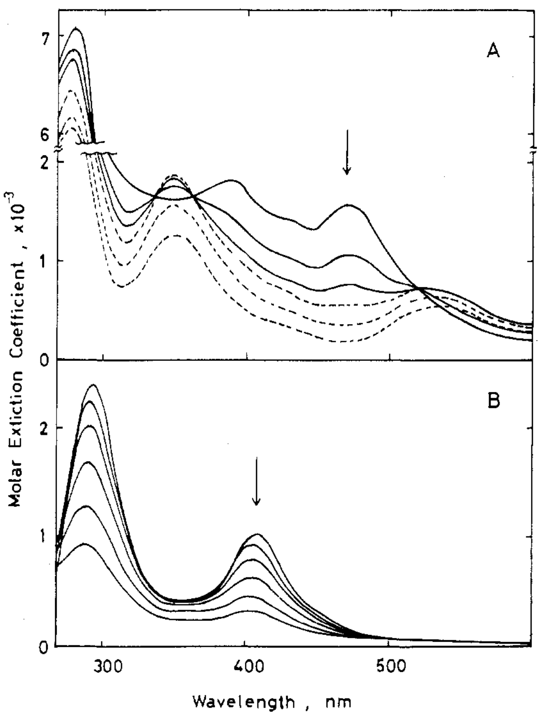

Figure 1. Spectral changes of 2.72×10^{-4} M cupric bromide (A) and chloride (B) as a function of water concentration in chloroform containing 0.20 M CTABr (A) or CTACl (B) at 25.0 °C. From top to bottom, water concentrations are 0.047, 0.213, 0.248, 0.287, 0.321, and 0.503 M in A and 0.60, 0.415, 0.569, 0.722, 0.874, and 1.024 M in B, respectively. The arrows indicate the direction of change as the water concentration is increased. Solid and broken lines in A indicate the difference in the color of the solution, brown and violet, respectively.

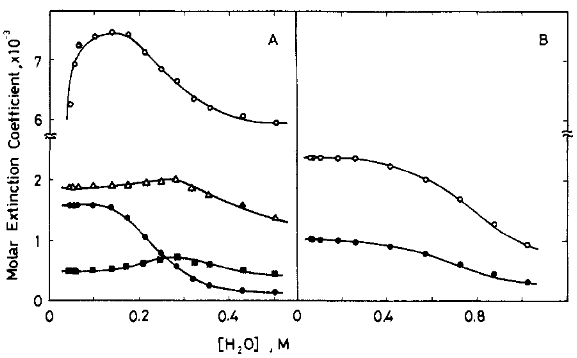

Figure 2. Changes of apparent extinction coefficients of cupric bromide (A) and chloride (B) in 0.20 M CTABr (A) or CTACl (B)/chloroform reversed micelles at 25.0 °C as a function of water concentration. The wavelengths used are 284 (○), 380 (△), 470 (●), and 530 nm (■) for CuBr$_2$ and 294 (○) and 408 nm (●) for CuCl$_2$.

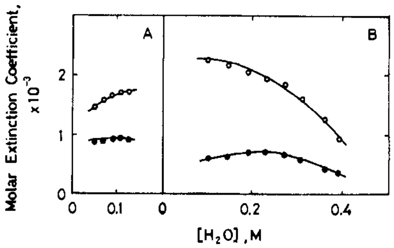

Figure 3. Changes of apparent extinction coefficients of cupric bromide (A) and chloride (B) in 0.20 M QDBr (A) or QDCl (B)/chloroform reversed micelles at 25.0 °C as a function of water concentration. The wavelengths used are 284 (○) and 470 nm (●) for CuBr$_2$ and 294 (○) and 408 nm (●) for CuCl$_2$.

of the band at 284 nm drastically increases with the increase in water concentration up to about 0.15 M. It seems unreasonable to discuss the conformation of complexes on the basis of spectral change in the ultraviolet region. Therefore, further discussion about this band was dropped. Addition of more water up to about 0.3 M brings about disappearance of all the three absorption bands with a concomitant appearance of two new bands at 340 and 530 nm. During this spectral change, tight isosbestic points are observed at 330, 360, and 520 nm (Figure 1A, solid lines). Further increase in water concentration up to 0.5 M also causes the decrease in intensities of these new bands (Figure 1A, broken lines). The intensity of each absorption band as a function of water concentration is given in Figure 2A. It is, hence, clear that there exists a two-step transformation in the system. For cupric chloride in the CTACl micelles, two absorption bands located at 294 and 408 nm are observed. Considering their locations and apparent extinction coefficients, they must correspond to the two bands of longer wavelength in the bromide, which may be assigned to the charge-transfer band. In the cupric chloride/CTACl system, spectral change is very small over the range of low water concentration (<0.2 M). However, very careful inspection of the spectra again revealed a transformation with isosbestic points at 398 and 333 nm, which is followed by the second one as evidenced by a steady decrease in the intensity of both absorption bands (Figures 1 and 2B).

Electronic absorption spectra of copper(II) complexes in the QDX/chloroform reversed micelles are essentially the same as those in the CTAX/chloroform micelles with several minor exceptions. First, the solubility of water into the QDX micelles, especially QDBr ones, is rather low compared with that into the CTAX counterparts. Therefore, the spectral change could be measured only over a limited range of water concentration (Figure 3). For cupric bromide, the apparent extinction coefficients of bands in QDBr reversed micelles were smaller than those in CTABr micelles when compared under identical conditions.

Detailed information on the d–d band of the copper(II) complexes in reversed micelles was difficult to obtain, because the weak d–d band of metal was largely obscured by the nearby strong absorption due to water (vide infra). When a relatively large amount of cupric chloride (8.8×10^{-3} M) was cosolubilized in the 0.20 M water/0.18 M chloroform micelles, however, a limited amount of information was obtained. A broad absorption band was observed at 1190 nm with an apparent extinction coefficient of 120 M^{-1} cm^{-1}, which is attributable to the d–d transition of copper(II) in a tetrahedral ligand field.[16,19] But, it is definitely different from that of mononuclear complex of copper(II) normally observed in the aqueous media containing a large amount of chloride ion, where a broad absorption is observed at 886 nm with an apparent extinction coefficient of 59 M^{-1} cm^{-1} in 4 M aqueous hydrochloric acid or 4 M sodium chloride solution. Upon the addition of water, the 1190-nm band shifted to a shorter wavelength with a concomitant decrease in the apparent extinction coefficient as shown in Figure 4. The band maximum is observed at 870 nm ($\epsilon_{870} = 25$ M^{-1} cm^{-1} at the highest water concentration, 2.3 M). It is close to that of fully hydrated copper(II) ion of distorted-octahedral configuration ($\epsilon_{824} =$ 12 M^{-1} cm^{-1}).[25] Hence, it is clear that a configurational change of the copper complex takes place over the range of water concentration studied.

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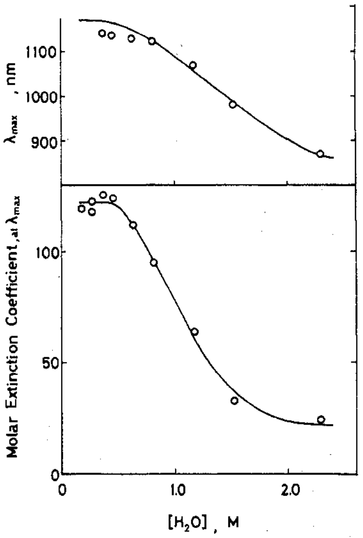

Figure 4. Changes of the ligand-field band of cupric chloride (8.8×10^{-2} M) as a function of water concentration in chloroform containing 0.20 M CTACl at 25.0 °C.

EPR Spectra. For characterization of the copper(II) complexes present in the cationic reversed micelles, EPR studies were carried out for 2.72×10^{-4} M cupric chloride in chloroform containing 0.20 M CTACl and different amounts of water. Surprisingly, no discernible signal deriving from copper(II) was observed between 25 and −15 °C, when the water concentration was lower than 0.5 M. At about 0.5 M water, the complex became EPR positive, and further addition of water made the signal more intense. As the temperature was lowered from 25 to −15 °C, the signal intensity increased as expected.[26] Figure 5A exhibits an EPR spectrum obtained at −15 °C for 2.72×10^{-4} M cupric chloride in 0.20 M CTACl/0.80 M water/chloroform micelles. The signal consists of a single broad band with $g = 2.21$, indicating an isotropic environment with respect to copper(II). When 1,1,2,2-tetrachloroethane was substituted for chloroform as the bulk solvent in the 0.20 M QDCl/0.44 M water/8.62×10^{-4} M cupric chloride system, a strongly anisotropic EPR spectrum was observed at −20 °C (Figure 5B). That there is no essential difference in the electronic spectra under consideration between the two different solvents employed was of course ascertained beforehand. The $g_{\parallel}$ and $g_{\perp}$ values were 2.241 and 2.003, respectively, at −20 °C. For confirmation that these EPR behaviors of the copper(II) complex in the cationic micelles are not caused by the freezing of water or whole solution itself or by phase separation, the apparent freezing point of water solubilized in reversed micelles was determined by employing an NMR technique.[4]

Near-Infrared Spectra. In reversed micellar systems a part of the solubilized water is located in the bulk organic phase where the water molecules are mostly free from hydrogen bonding among themselves, and other water interacts with the ionic head of surfactant and/or polar solutes cosolubilized in the interior of micelles. In the near-infrared region, the former exhibits an absorption band around 1900 nm and the latter over a range of 1920–2020 nm.[4,7] The configuratin of the copper(II) complexes in reversed micelles is drastically affected by the amount of water present. The addition of metal ion is expected to draw water molecules into the interior core of micelles from the bulk phase.[27] However, even when 8.8×10^{-3} M cupric chloride was present in the 0.20 M CTACl/0.18 M water/chloroform micelles,[28] no significant change in the near-infrared spectrum of water was observed.

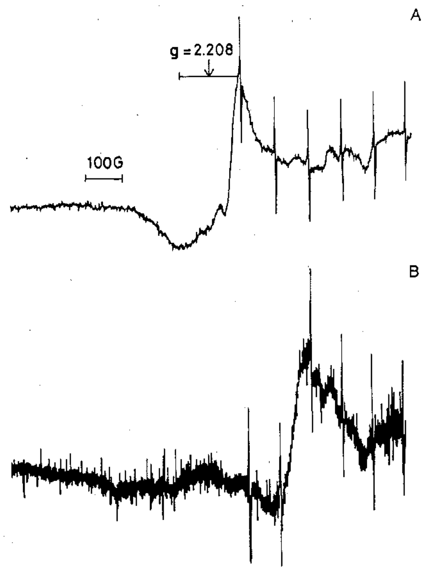

Figure 5. EPR spectra of 2.72×10^{-4} M cupric chloride in 0.20 M CTACl/0.83 M water/chloroform reversed micelles at −15 °C (top) and of 8.62×10^{-4} M cupric chloride in 0.20 M QDCl/0.14 M water/1,1,2,2-tetrachloroethane reversed micelles at −20 °C (bottom).

Discussion

Structure of Cupric Halides Cosolubilized in Reversed Micelles. As is well-known, the cupric ion exists in a hexahydrated and distorted-octahedral configuration in a dilute aqueous medium.[25] Addition of excess chloride ion leads to a formation of such hydrated complexes as $CuCl^+$, $CuCl_2$, $CuCl_3^-$, and $CuCl_4^{2-}$, and electronic spectral properties of these species have also been established rigorously.[21] For example, the predominant species at a high chloride concentration, $CuCl_4^{2-}$, has three absorption bands in the UV–visible region, i.e., 240, 265–270, and 370–380 nm. However, a relationship between these absorption bands and the structure of the complex is not clearly understood. Helmholz and Kruh argue that $CuCl_4^{2-}$ takes a distorted-tetrahedral configuration (D_{2d} symmetry) in an aqueous medium from the similarity of its absorption spectrum ($\lambda_{max} = 380$ nm) to that of crystalline Cs_2CuCl_4 ($\lambda_{max} = 416$ nm).[11] On the other hand, Eswein et al. favor a square-planar configuration (D_{4h} symmetry) for the same complex because of lack of the band at 450 nm, characteristic of D_{2d} configuration.[22] In addition, the formation of polynuclear copper(II) complexes is likely to take place even in solution.[24] According to the intensive work by Willett et al. on the crystalline cupric chloride, the planar complexes being in a dimeric or trimeric form are expected to show a characteristic band at about 526 nm.[17,18]

Taken altogether, it is certain that the copper(II) halide complexes present in the cationic reversed micelles containing a relatively small amount of water are quite different from those in solutions hitherto reported. The most probable candidate for the complexes present in reversed micelles containing a very small amount of water is likely to be polynuclear cupric halide complexes with a distorted-tetrahedral structure, which is certainly evidenced by the existence of the band at 408 nm. That the complex gives no EPR signal under usual conditions is further evidence in favor of this contention. This is indicative

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(28) This is the highest concentration of cupric chloride attainable under the present conditions.

Scheme I

species :	$[\mathrm{Cu}{<}^{X}_{X}{>}\mathrm{Cu}]_n^{2-}\cdot 2R_4\overset{+}{N}$ polynuclear, bridged by halogens	$\underset{\text{heating}}{\overset{H_2O}{\rightleftharpoons}}$	$[Cu(H_2O)_nX_{m-n}]^{1+\sim 2-}$ monomeric, ex, $CuCl_4{}^{2-}$, $CuCl_3(H_2O)^-$, or $CuCl(H_2O)_3{}^+$	$\overset{H_2O}{\rightleftharpoons}$	$[Cu(H_2O)_6]^{2+}\cdot 2X^{2-}$ monomeric
configuration :	distorted tetrahedral (D_{2d}) or square planar (D_{4h})		distorted tetrahedral (D_{2d})		tetragonally distorted octahedral (Oh)
color of micellar solution :	yellow or brown		violet or redish violet		blue
$\frac{[H_2O]}{[\text{detergent}]}$ ratio in micelles :	less than about unity		about 2 - 4		larger than about 4

of the spin–spin-exchange interaction between the neighboring copper(II) ions in polynuclear complexes.[10,15] On the other hand, the fact that the yellow solution of the cupric chloride/QDCl/water/tetrachloroethane micelle is EPR positive at −20 °C (Figure 5B) reasonably suggests that the spin–spin exchange between the neighboring copper(II) nuclei in the polymer is prohibited by lowering temperature.[26] Another possibility is the formation of the polymeric $CuCl_6$ complex of D_{4h} symmetry. Because the complex is known to show a d–d band with a small extinction coefficient ($\epsilon \sim 10$) around 800 nm,[10] however, this alternative structure should be ruled out.

Through X-ray diffraction studies on the concentrated aqueous solution of cupric chloride (3.18–4.35 M), Wertz and co-workers have demonstrated the formation of polynuclear chloroaquo complexes of copper(II).[24] Our present system resembles theirs where the local cupric chloride concentration is relatively high. In the system of 0.20 M CTACl/0.20 M water/chloroform, for example, CTACl will exist as an intimate or undissociated ion pair.[4] Therefore, chloride ion of the surfactant does not seem to play a role as an effective ligand for copper(II). In addition, since cupric chloride is confined only in a small domain (polar interior core) of the micelles, it is some 280 times more concentrated locally. This is probably the lowest estimation for the local salt concentration, because most of the water is bound to the ionic head of surfactant and is not available to solvating cupric chloride[4,7] (vide infra). Under the circumstances, the polymeric species will be easily formed. In this situation, water present in the system also may not coordinate to the metal, which is evident in the near-infrared spectrum of water. If water coordinated to the metal, an additional absorption band of water derived from the hydrated copper(II) species such as $Cu(H_2O)_nCl_{m-n}$ should have been observed in the near-infrared region. Therefore, it may be reasonable to consider that, even when a divalent metal ion is present in the reversed micelles, water predominantly interacts with the ionic head group of surfactants at the first stage.[4,7] The configurational change of copper(II) halides in a specific field of reversed micellar core is summarily represented in Scheme I.

Effect of Water Concentration: Solvochromism. With the increase in water concentration, the water pool of micelles expands,[5] and the solubilized water molecules become available for the coordination to the cosolubilized metal ion. As expected from our previous finding about the behavior of Co(II) complexes in reversed micelles,[7] solvochromism of the copper(II) complexes with water was observed also in the present system. With further increase in the water concentration (up to about 0.20 M) in the 2.72 × 10^{-4} M cupric bromide/0.20 M CTABr/chloroform system, the yellow solution turned violet, indicating the transformation from the distorted-tetrahedral polynuclear complexes to the similar monomeric species. Under the circumstances, adding water will disrupt the halogen bridge of polymer to give monomers of mixed-ligand complexes with halogen and water, i.e., $Cu(H_2O)_nCl_{m-n}$. Adding more water eventually leads to the formation of fully hydrated copper(II) ion. Considering that the distorted-tetrahedral complexes of copper(II) are usually EPR negative, the fact that an EPR signal was observed at relatively high water concentration (about 0.8 M) is suggestive of the formation of the tetragonally distorted-octahedral species. When the counterion is bromide in both CTAX and QDX micelles, the solvochromic configurational change of copper(II) complexes as a function of water concentration more easily occurs compared with the chloride case. The difference in the ease of solvochromism between both halides is explained in terms of the electronegativity and the ligand field theory.

Effect of Temperature: Thermochromism. When 0.56 M water is added to the system containing 2.72 × 10^{-4} M cupric bromide and 0.20 M CTABr in chloroform at 25.0 °C, the yellow solution fades (Figure 2A). Then, on warming of the resulting solution up to 50.0 °C, the yellow color is reproduced and intensified with the increase in temperature (Figure 6). The spectral change effected by temperature was just like the mirror image of solvochromism caused by water. The spectral change is completely reversible thermotropically. This is also similar to the previous finding for the cobalt(II) complexes.[7] The thermochromism can be elucidated in terms of the same principle as that considered for solvochromism. Water solubilized in reversed micelles usually locates both in the bulk organic phase and in the interior core of micelles.[4,7] Raising the temperature leads to the increase in the mobility of water bound to surfactants and in the solubility of water into the bulk organic phase.[4,7] As the temperature is raised, therefore, an amount of water present in the micellar core decreases with a concomitant increase of that of water locating in the bulk phase. This is clearly revealed in the near-infrared spectra of O–H vibrational modes of water.

In any event, the most important thing of the present findings is the formation of polynuclear complexes bridged by

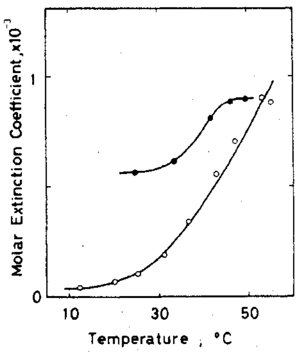

Figure 6. Thermochromism of cupric bromide (○) in 0.20 M CTABr/0.56 M water/chloroform reversed micelles as monitored at 470 nm and of cupric chloride (●) in 0.20 M CTACl/0.83 M water/chloroform reversed micelles as monitored at 408 nm.

halogens in solutions containing water. The amount of water present in the overall system was always sufficient enough to hydrate the copper(II) ion. Nevertheless, in the range where the concentration ratio of water to detergent is relatively small, solubilized water is predominantly interacting with detergents even if other polar solutes are cosolubilized in the system.[4,7] The specific phenomenon is explained in terms of "the two-step hydration mechanism" in the reversed micellar system.[4,7] In addition, the copper(II) halides are encapsulated into a very small polar domain surrounded by bulk nonpolar phase, which causes the increase in the local concentration of the complex.

Masui et al. were the first to investigate the behavior of paramagnetic metal complexes in reversed micelles by means of EPR spectroscopy.[29] In their work the cupric chloride/dodecylpyridinium chloride/chloroform system was adopted. However, the EPR spectrum of copper(II) determined at a relatively low water concentration (the actual concentration was not given) is different from ours. Considering that the electronic spectra of their system showed an absorption band at 406 nm, very close to ours (408 nm), chloride ion must be the most probable ligand also in their system. Therefore, the EPR spectral difference between their and our systems should be interpreted in terms of the microscopic viscosity in the micellar core, which governs the ease of molecular motion of the complex cosolubilized therein.

Acknowledgment. The authors are indebted to Kao Soap Co. for a supply of the starting materials needed for the synthesis of surfactants.

Registry No. $CuCl_2$, 7447-39-4; $CuBr_2$, 7789-45-9.

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Kinetics and Mechanism of Aquation and Formation Reactions of Carbonato Complexes. 18. Carbon Dioxide Uptake by and Decarboxylation of the *trans*-Bis(ethylenediamine)rhodium(III) System in Aqueous Solution[1]

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Received April 18, 1980

The new (carbonato)bis(ethylenediamine) complexes of rhodium(III) *trans*-$[Rh(en)_2(OCO_2)(OH_2)]ClO_4$ and *trans*-$Na[Rh(en)_2(OCO_2)_2]$ have been prepared, the former in the pure solid state and the latter in solution containing excess carbonate. The rate parameters for acid-catalyzed decarboxylation of the *trans*-aquocarbonato species are $k_1 = 2.92 \pm 0.08$ s^{-1} at 25 °C. $\Delta H_1^\ddagger = 10.9 \pm 0.1$ kcal mol^{-1} and $\Delta S_1^\ddagger = -19.6 \pm 0.4$ cal deg^{-1} mol^{-1}. The *trans*-dicarbonato analogue undergoes complete decarboxylation at pH ≤6 in a one-step process to produce the expected equilibrium mixture of *trans*-diaquo and *trans*-aquohydroxo species, with $k_5 = 2.26 \pm 0.05$ s^{-1} at 25 °C, $\Delta H_5^\ddagger = 16.3 \pm 0.2$ kcal mol^{-1}, and $\Delta S_5^\ddagger = -2.1 \pm 0.8$ cal deg^{-1} mol^{-1}. At higher pH (>6.5), only one of the carbonato groups is eliminated to produce a mixture of *trans*-$Rh(en)_2(OCO_2)(OH_2)^+$ and *trans*-$Rh(en)_2(OCO_2)(OH)$, with $k_3 = 1.3 \pm 0.1$ s^{-1} at 25 °C, the only temperature at which this constant was determined. Carbon dioxide uptake by *trans*-$Rh(en)_2(OH)(OH_2)^{2+}$ and *trans*-$Rh(en)_2(OCO_2)(OH)$ yield *trans*-$Rh(en)_2(OCO_2)(OH_2)^+$ and *trans*-$Rh(en)_2(OCO_2)_2^-$, respectively, with second-order rate constants at 25 °C of $k_2 = 81 \pm 3$ and $k_4 = 330 \pm 80$ M^{-1} s^{-1} and the activation parameters $\Delta H_2^\ddagger = 12.9 \pm 0.9$ kcal mol^{-1} and $\Delta S_2^\ddagger = -5.5 \pm 3.1$ cal deg^{-1} mol^{-1} and $\Delta H_4^\ddagger = 15.4 \pm 0.7$ kcal mol^{-1} and $\Delta S_4^\ddagger = 4.6 \pm 2.4$ cal deg^{-1} mol^{-1}. An unusual aspect of this study is the finding that CO_2 uptake by *trans*-$Rh(en)_2(OH)_2^+$ is a third-order process which yields the dicarbonato species *trans*-$Rh(en)_2(OCO_2)_2^-$ in a single step, with $k_6 = (1.4 \pm 0.2) \times 10^4$ M^{-2} s^{-1}, $\Delta H_6^\ddagger = 16.3 \pm 0.9$ kcal mol^{-1}, and $\Delta S_6^\ddagger = +16.4 \pm 3.0$ cal deg^{-1} mol^{-1}. These and the other results of this investigation are compared and discussed in relation to previous findings for analogous Co(III) and Rh(III) systems.

Introduction

In the preceding paper in this series[1] we reported on the carbon dioxide uptake by and decarboxylation of the analogous *cis*-bis(ethylenediamine)rhodium(III) system in aqueous solution. Two new carbonato complexes were reported, viz., the bidentate carbonate species *cis*-$Rh(en)_2(CO_3)^+$ and the monodentate species *cis*-$Rh(en)_2(OCO_2)(OH_2)^+$. Acid-catalyzed decarboxylation of the ring-closed species, which necessitates metal–oxygen bond breaking, is very slow due to the strength of the Rh–O bond in this complex. On the other hand, the *cis*-$Rh(en)_2(OCO_2)(OH_2)^+$ species undergoes rapid decarboxylation for which the kinetic parameters are very

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[1] Part 17: Palmer, D. A.; van Eldik, R.; Kelm, H.; Harris, G. M. *Inorg. Chem.* **1980**, *19*, 1009.

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0020-1669/80/1319-3673$01.00/0