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Speciation of Ternary Cobalt(II) Phenanthroline−Silica Surface Complexes as a Function of pH and Ligand Steric Bulk

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Co(II) solution species containing 1 equiv of phenanthroline (phen), 2-methyl-1,10-phenanthroline (MMP), or 2,9-dimethyl-1,10-phenanthroline (DMP) ligand formed inner-sphere surface complexes when grafted on silica. The speciation on the silica surface depended on both the pH of the grafting solution and the steric bulk of the ligand. $[Co(DMP)]^{2+}$ formed tetrahedral surface adducts exclusively, with a 1:1 ligand−Co ratio. These surface adducts were first detectable at pH values above 5.1. $[Co(MMP)]^{2+}$ and $[Co(phen)]^{2+}$ formed exclusively octahedral adducts on the surface with a 1:1 ligand−Co ratio at pH values below 5. The $[Co(MMP)]^{2+}$ complex formed a tetrahedral adduct initially at pH 6 and increasingly as the pH was raised. The $[Co(phen)]^{2+}$ complex did not produce a comparable tetrahedral surface species under any conditions. Instead, mixtures of octahedral surface species with both 1:1 and 2:1 ligand−Co ratios began to form at pH values above 6. Taken together, the results indicated that the development of tetrahedral stereochemistry was strongly influenced by steric factors in the presence of a nitrogen-donating ligand. All three phenanthroline derivatives promoted surface binding of the Co(II) ion adducts, so that maximal binding occurred at lower pH values than for binding of $[Co(H_2O)_6]^{2+}$, which formed exclusively tetrahedral adducts.

Introduction

The fields of inorganic and surface chemistry have become increasingly intertwined due to a common interest in producing heterogeneous transition metal catalysts.[1−8] Many of the studies reporting heterogeneous catalysis lack detail regarding the identity of the active surface species as well as the effect of surface speciation on catalytic activity. This level of detail is particularly important when the intentions of such studies are to deduce a mechanism and thus to improve the performance of supported catalysts.

Recent work in this laboratory has produced a clear structural picture of an unusually homogeneous distorted tetrahedral adduct that forms when the solution complex $[Co(2,9\text{-dimethyl-1,10-phenanthroline})]^{2+}$ ($[Co(DMP)]^{2+}$) binds to silica gel surfaces.[9] A surface species having a single silanol bond was characterized by X-ray absorption spectroscopy (XAS), IR, UV−vis, and pH titration data, which were consistent with the formula $[Co(DMP)(SiO)(H_2O)](NO_3)$. The concentration of the tetrahedral adduct on the surface was increased concomitantly with the pH of the grafting solution within the pH range 5−8. An increase in spectral intensity by 16-fold and the unique characteristic spectrum of the surface adduct relative to the octahedral solution precursor, $[Co(DMP)(H_2O)_4](NO_3)_2$, allowed for the probing of a variety of silica surfaces.

The $[Co(DMP)]^{2+}$ silica surface adduct has shown catalytic activity toward the disproportionation of hydrogen peroxide (catalase activity) in this laboratory.[10] Catalase activity has also been observed previously for $[Co(phen)]^{2+}$ and $[Cu(phen)]^{2+}$ complexes grafted on alumina[11] and for

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cobalt and copper diimine and aminopyridine adducts grafted on or adsorbed to ion-exchange resins and silica gel, respectively.[12-14] In the previous studies, qualitative observations of color indicated that the most likely coordination modes at the surfaces were octahedral and tetrahedral, respectively.[11-13] Inferences regarding mechanism or changes in catalytic activity were limited because of the inherent ambiguities associated with the superficial characterization of the polymer-bound metal centers.

The overall goal of this work was to clarify whether metal-ion stereochemistry has a significant influence on the catalase activity of the surface-bound complexes, with the ultimate intention of applying these insights to studies of other catalysis systems. In our previous study, the decrease in coordination number when the $[Co(DMP)]^{2+}$ fragment bound to silica gel was attributed to steric interactions between the methyl groups of the DMP ligand and the silica surface.[15-17] Accordingly, it was expected that examination of a series of cobalt phenanthrolines with incremental changes in steric bulk around the metal binding sites would help to confirm this hypothesis and would provide insight into the steric effects on surface stereochemistry that could be applied to the understanding of catalytic behavior. As described in this work, we have found that the tuning of steric effects about the periphery of the phenanthroline metal binding site does indeed have a strong influence on both the affinity and stereochemistry of surface binding for the Co(II) complexes, although differences in the surface speciation behavior associated with the various ligands precludes direct comparison of the catalytic chemistry.

Experimental Section

General. Unless otherwise stated, all chemicals were of reagent grade and used as received from Aldrich. 2-Methyl-1,10-phenanthroline, MMP, was prepared by methylation of phenanthroline as described below. Silica gel (Merck 9385) was washed with 6 M HCl and then rinsed with distilled water during vacuum filtration. The washing procedure was repeated several times until the washing solution was neutral to universal pH indicator paper and the yellow color resulting from ferric ions present in the sample was no longer visible by inspection. The silica was then dried in a 50 °C oven overnight and stored in a closed bottle on the benchtop. pH measurements were made using a Corning ion/pH analyzer 350 and ion selective electrode. Proton NMR spectra were obtained using a 300 MHz Varian Mercury spectrometer. Visible spectral measurements were made on a Hewlett-Packard 8452A diode array spectrophotometer using 1-cm path length quartz cuvettes for solutions. Measurements on the solid silica samples were performed using the same spectrometer equipped with a Labsphere RSA-HP-84 diffuse reflectance accessory and a BR21A reflectivity reference (Labsphere) as the background. Spectra for silica samples were obtained in transmittance mode and converted using the Kubelka−Munk function $[(1 - F_T)^2/(2F_T)]$, where F_T = fraction transmitted.[18]

2-Methyl-1,10-phenanthroline. 1,10-Phenanthroline (0.57 g, 3.16 mmol), 1,4-diazabicyclo[2,2,2]-octane (DABCO) (0.9 g, 8.02 mmol), and 40 mL of dry benzene were added to a flame-dried 100-mL Schlenk flask and cooled to 5−10 °C in a salt/ice water bath. Methyllithium (1 M in cumene/tetrahydrofuran, 12 mL, 12 mmol) was added dropwise over 20 min. The mixture was stirred at 5−10 °C for 30 min and then allowed to warm to room temperature. The dark red-brown mixture was quenched with an equal volume of saturated aqueous ammonium chloride and extracted with ether (3 × 50 mL). The ether extracts were combined, washed with 100 mL of brine, and dried over anhydrous sodium sulfate. The solvents were removed under reduced pressure, affording the crude product as a yellow oil. The crude product was redissolved in 150 mL of dichloromethane, then 200 mL of 1:1 bleach−water and 0.10 g of tetrabutylammonium hydrogen sulfate were added. After the mixture was stirred vigorously overnight, the organic layer was collected and washed with water (2 × 50 mL) and then brine (50 mL). The resulting yellow oil was then dried over anhydrous sodium sulfate and purified by column chromatography on silica gel (230−400 mesh 60 A) using 60% ethyl acetate, 38% hexanes, and 2% triethylamine as the eluting solvent ($R_f = 0.11$). The oily product was crystallized by dissolving in ether and adding hexanes (yield 0.47 g, 77% overall). Mp = 88−89 °C. ^1H NMR ($CDCl_3$/TMS, δ): 2.92 (s, 3H), 7.50 (d, 1H), 7.65 (m, 2H), 7.75 (m, 1H), 8.10 (d, 1H), 8.21 (d, 1H), 9.21 (d, 1H).

Determination of Surface Binding. A 0.1 M aqueous stock solution of $[Co(NO_3)_2\cdot 6H_2O]$ (J.T. Baker) and 0.1 M methanol stock solutions of each ligand (phen, MMP, and DMP) were prepared. Immediately prior to each experiment, the ligand and cobalt stock solutions were combined by diluting 5 mL of each to a total volume of 100 mL with distilled H_2O to make a 0.005 M solution with 1:1 ligand−metal ratio. Methanol was added in place of the ligand stock for the pH titration preformed in the absence of added ligand. Cleaned Merck silica gel 9385 (1.00 g, reported surface area approximately 480 $m^2\ g^{-1}$ and pore diameter 60 Å), weighed at ambient temperature and humidity, was added to 10 or more flasks for each of four data sets using phen, MMP, DMP, and nitrate cobalt adducts. Aliquots of 2 mL of 0.1 M HCl and 2 mL of 1 M sodium nitrate were added to each flask containing the silica. The pH was increased incrementally from one flask to the next within the range of 2 to ∼10 by addition of 10 mL of various dilutions of a 0.1 M NaOH solution. $[Co(ligand)]^{2+}$ or $[Co(H_2O)_6]^{2+}$ (8 mL, 0.005 M) was then added to each flask. The final concentration in each silica slurry was 0.009 M HCl, 0.09 M $NaNO_3$, and 0.0018 M $[Co(ligand)]^{2+}$ or $[Co(H_2O)_6]^{2+}$. The samples were incubated at 25 °C for 3 h, during which time mixing was accomplished by physically shaking the samples every few minutes. The pH of the supernatant was measured after incubation. The pH was not adjusted after the 3-h period; rather, the desired pH was achieved by preliminary experiments establishing the starting pH values that gave the greatest number of points in the pH range of interest. Samples incubated overnight showed little to no variation in the amount of grafted Co^{2+}. The pH titration data presented for the $[Co(DMP)]^{2+}$ represent only one data set as the $[Co(DMP)]^{2+}$ titration data agreed very well with those data reported earlier at a higher grafting concentration.[9] The pH titration data for $[Co(MMP)]^{2+}$, $[Co(phen)]^{2+}$, and $[Co(H_2O)_6]^{2+}$ represent the average of two data sets (error bars

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omitted for clarity, included in Supporting Information (SI) Figures S1−S3).

The concentration of grafted [Co^{2+}] was determined for $[Co(MMP)]^{2+}$, $[Co(DMP)]^{2+}$, and $[Co(H_2O)_6]^{2+}$ grafted silica samples by first removing a known volume from the grafting solution. The solutions removed were then adjusted to a pH below 7 and diluted appropriately with 15% NH_4SCN in acetone. The NH_4SCN/supernatant v/v ratio was maintained at 75%.[19] A linear working curve for $[Co(NCS)_4]^{2-}$ was established in the absorbance range of 0.2 to 1 ($\epsilon = 1841$ M^{-1} cm^{-1} at 622 nm) both in the presence and in the absence of MMP and DMP ligands. Independent measurements produced at most an error of 5%. The concentration of Co^{2+} grafted on the surface was calculated by subtracting the amount remaining in solution from the initial concentration added.

For the $[Co(phen)]^{2+}$ samples, a different assay was developed because the thiocyanate anion did not compete efficiently with phenanthroline. $[Co(phen)]^{2+}$ was converted to $[CoCl_4]^{2-}$ by first freeze-drying known volumes (5 mL or 10 mL) of the grafting solutions that were placed in 15 mL eppendorf tubes covered with perforated caps. A Labconco Freeze-Dry System/Freezone 4.5 instrument was used for lyophilization. The freeze-dried samples were then treated with either 0.25 or 0.5 mL of deionized H_2O (to aid in the dissolution of the salt), followed by 5 or 10 mL of 12 M HCl. The nitrate salts present from the grafting solution did not completely dissolve in the concentrated HCl and thus were allowed to settle after thorough mixing of the samples. The supernatant was removed from each sample and the $[CoCl_4]^{2-}$ was determined spectrophotometrically. A linear working curve, established for the spectrophotometric assay within the range of 0.1 and 0.5 AU, gave $\epsilon = 570$ M^{-1} cm^{-1} at 692 nm.

An assay was also developed for the determination of MMP and phen ligand concentrations in the supernatant solutions. Given the thorough characterization of the DMP adduct in the previous work,[9] this assay was not performed for the DMP ligand. A linear working curve for the $\pi \rightarrow \pi^*$ transitions of the protonated ligands in concentrated HCl solutions produced $\epsilon = 35\,300$ and $35\,900$ M^{-1} cm^{-1} at 282 and 280 nm for MMP and phen, respectively. Because of the large extinction coefficients of the $\pi \rightarrow \pi^*$ transitions relative to that of the d−d transition used for determining cobalt, it was necessary to perform serial dilutions on the samples in order to obtain readings within a linear range. Consequently, the error associated with the ligand assay is higher than that for the cobalt determinations. On the basis of a working curve prepared using identical dilutions from a concentrated stock solution, a maximum error of ~7% was established for the phenanthroline concentrations vs a 5% error for the cobalt concentrations. Select samples were also treated with excess (2×10^{-3} M) Co^{2+} in sodium acetate buffer (pH 5) in accord with a previously published method.[20] The absorptivities of these samples at $\lambda_{max} = 270$ nm ($35\,900$ M^{-1} cm^{-1}) were comparable to those obtained at 280 nm for the same samples treated with HCl, although the absorption coefficient ($33\,000$ M^{-1} cm^{-1}) was found to be slightly higher than that reported by Park and Jung.[20]

Results and Discussion

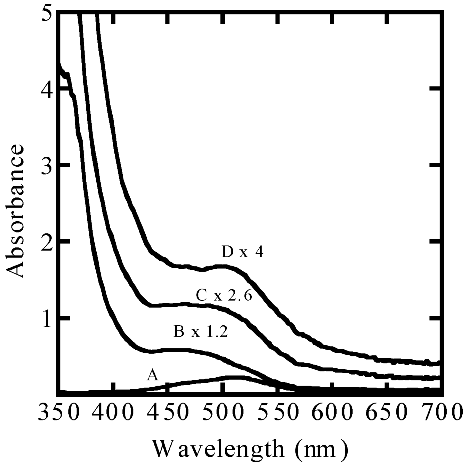

Figure 1. The visible solution spectra of 0.043 M $[Co(H_2O)_6]^{2+}$ ($^1/_4$ dilution of a 10 000 mg/mL Ultra Scientific atomic adsorption standard at pH 1) (A) and 0.03 M Co^{2+} in the presence of one equivalent phenathroline (B), 2-methyl 1,10-phenanthroline (C), and 2,9-dimethyl-1,10-phenanthroline (D). Spectra B, C, and D are multiplied by the factor shown for clarity and were measured at an ambient pH of ~6.

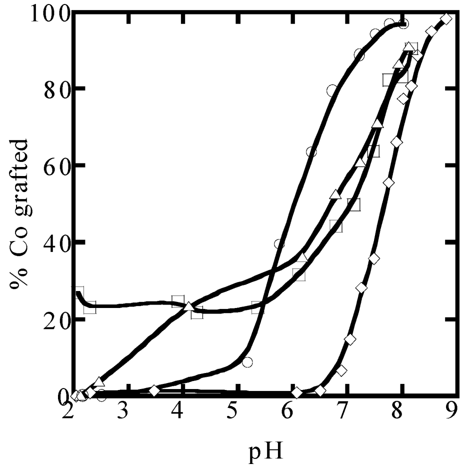

Figure 2. The amount of Co^{2+} grafted on 1 g of Merck 9385 silica as a function of solution pH using aqueous complexes $[Co(H_2O)_6]^{2+}$ (diamonds), $[Co(phen)(H_2O)_4]^{2+}$ (squares), $[Co(MMP)(H_2O)_4]^{2+}$ (triangles), and $[Co(DMP)(H_2O)_4]^{2+}$ (circles). The lines shown are smooth fits to two data sets per grafting species.

Mixtures of $[Co(NO_3)_2{\cdot}6H_2O]$ and phenanthroline (phen), 2-methyl-1,10-phenanthroline (MMP), or 2,9-dimethyl-1,10-phenanthroline (DMP) (1:1) in aqueous methanol solutions all produced similarly shaped broad spectra with maxima at approximately 460, 486, and 500 nm (Figure 1, curves B, C, and D). These spectral features are typical of octahedral species and very similar to that of aqueous $[Co(NO_3)_2{\cdot}6H_2O]$, which exhibits a single absorption maximum centered at approximately 510 nm (Figure 1, curve A: $\epsilon = 9$ M^{-1} cm^{-1}). Preedge X-ray absorption near edge structure analysis has supported a distorted octahedral structural assignment to $[Co(DMP)(H_2O)_4](NO_3)_2$, as described previously.[9]

Acid/base titrations with solutions of cobalt nitrate and the 1:1 complexes of Co^{2+} with DMP, MMP, or phen in the presence of silica afforded the curves shown in Figure 2. The data represent the total amount of cobalt detected on the silica surface for each species as a function of the grafting pH but do not provide information on the structural homogeneity of the surface species.

Surface Binding of Co^{2+}. In the absence of phenanthroline ligands, aqueous Co^{2+} became grafted on the silica surface over a pH range of ~7 to 8.8(Figure 2). Over 95% of the

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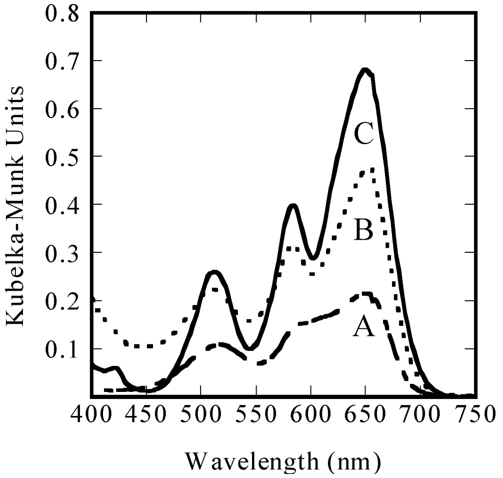

Figure 3. Diffuse reflectance spectra of $[Co(H_2O)_6]^{2+}$ (A) and Co^{2+} complexes grafted in the presence of 1 equiv of MMP (B) and DMP (C). Curves A, B, and C correspond to grafting pH values of 8.4, 8.1, and 8.0 and loadings of 1.8, 1.7, and 1.6 × 10^{-3} mol of Co^{2+}/g of silica, respectively. λ_{max} = 654, 584, and 512 nm (DMP and MMP adducts) and 650, 522, and ca. 592 nm (sh) (nitrate adduct).

solution species was accounted for on the silica surface at pH 8.8. A homogeneous distribution of tetrahedral surface sites was evident from the increase in diffuse reflectance spectral intensity without a change in spectral band shape (Figure 3, curve A, SI Figure S4) with λ_{max} = 650 and 522 nm and a shoulder centered at approximately 592 nm. The cobalt species are sensitive to moisture loss, as samples dried at 50 °C or in a desiccator overnight produced spectra that displayed less splitting in the visible region, due to a shift in the higher energy peak from 522 to 540 nm. The spectra produced after drying strongly resembled those of calcined sol−gel samples containing cobalt(II) nitrate.[21,22] The lower intensity of the diffuse reflectance spectrum compared to that of the tetrahedral $[Co(DMP)]^{2+}$ sample at similar loading (vide infra) suggested that the air-dried grafted cobalt samples have a five-coordinate structure,[23] with the fifth ligand most likely being a coordinated water molecule.

Surface Binding of $[Co(DMP)]^{2+}$. For the DMP adduct, the diffuse reflectance spectra indicated an increase in spectral intensity throughout the pH titration without a change in spectral shape (Figure 3, curve C, SI Figure S5), as was observed for the nitrate adduct (vide supra).

The pH data represented in Figure 2 are in agreement with our previous work,[9] which established that binding of $[Co(DMP)]^{2+}$ to the silica surface resulted in a homogeneous distribution of a highly distorted tetrahedral symmetric species at all grafting pHs.[24]

Surface Binding of $[Co(MMP)]^{2+}$. The MMP adduct became bound to the silica surface initially at pH 2.5 and substantially (20%) at pH 4.1, a range in which little to no surface binding was observed for the DMP cobalt adduct (Figure 2). The diffuse reflectance spectra for samples of the MMP adduct grafted at pH values of 2.5 and 4.1 showed the characteristic spectrum of an octahedral species. Beginning at pH 6 until maximal binding (~pH 8), the diffuse reflectance spectra clearly indicated the presence of a tetrahedral adduct (Figure 4). The three maxima of the MMP complex spectrum at 654, 584, and 512 nm were identical to those of the DMP adduct (Figure 3, curve B). The small spectral feature that appeared at 420 nm in the spectrum of the DMP adduct was not observed due to a significant intensity contribution from a species that absorbed at higher energy, which was believed to be an octahedral surface adduct (Figure 3, curves B and C). The spectral intensities at 654 nm for the DMP and MMP adducts at >90%-bound Co^{2+} were 0.68 and 0.47 Kubelka−Munk units, respectively, suggesting that approximately 30% of the cobalt is bound in an octahedral form in the presence of MMP.

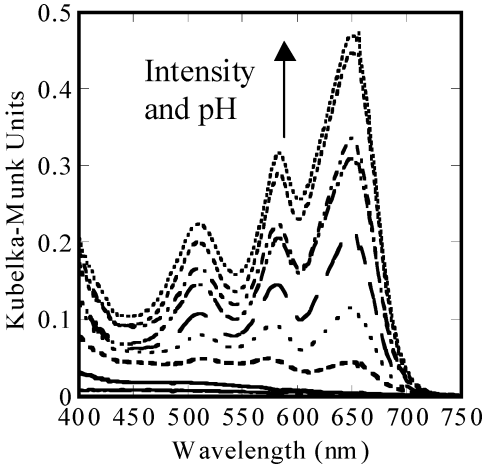

Figure 4. Diffuse reflectance spectra of Co^{2+} complexes grafted in the presence of 1 equiv of MMP at grafting pH values of 2.1, 2.5, 4.1, 6.0, 6.7, 7.3, 7.6, 7.9, and 8.1. The spectra correspond roughly to data points presented in Figure 2 that show the average values of two data sets.

An assay of the surface-bound MMP ligand over the pH range at which Co^{2+} was adsorbed indicated an approximately 1:1 ligand−Co ratio for all surface adducts above pH 4. Co^{2+} was not detected on the surface at pH 2, but about 20% of the ligand present was absorbed to the silica. Approximately the same percentage of MMP ligand bound to silica in the absence of cobalt at this pH (data not shown). A disproportionate amount of ligand binding at low pH values relative to Co^{2+} is consistent with the observations of other researchers for the phenanthroline ligand.[20]

Surface Binding of $[Co(phen)]^{2+}$. The cobalt−phen adduct became grafted to the silica surface at very low pH values relative to the MMP and DMP complexes (Figures 2 and 5). Equivalent amounts of Co^{2+} (~20%) were bound to the surface at grafting pH values between 2 and 5. The diffuse reflectance measurements produced virtually identical spectra for these samples with indistinguishable intensities (samples grafted at pH values of 2.0, 2.3, and 3.8 shown in Figure 5), suggesting a pH-independent binding in this pH range. Because Co^{2+} does not bind significantly to the surface

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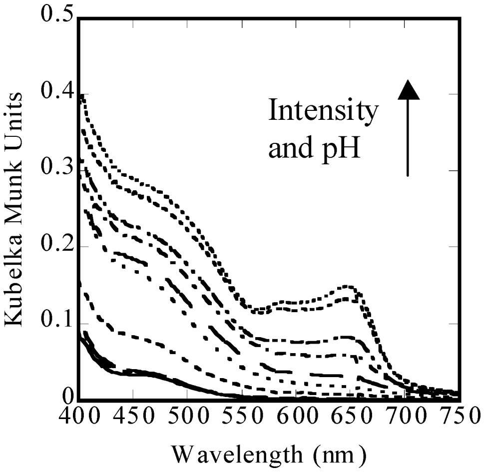

Figure 5. Diffuse reflectance spectra of Co^{2+} complexes grafted in the presence of 1 equiv of phen at pH values of 2.1, 2.3, 3.8, 6.4, 6.7, 7.0, 7.6, 7.9, 8.1, and 8.3. The spectra correspond roughly to data points presented in Figure 2 that show the average values of two data sets. Samples prepared at a grafting pH values of 2.1, 2.3, and 3.8 appear stacked on one another with equal intensities of approximately 0.5 units at 460 nm.

at pH values below 7 in the absence of phenanthroline ligands (Figure 2), the data suggest an octahedral 1:1 phen−Co surface adduct formed at the pH values under 5. Given that the amount of bound complex is essentially constant over this pH range and that deprotonation of silanol groups occurs primarily in the pH range 6−8,[25] the data most probably indicate association of the complex via interactions with protonated silanol groups (Si−OH).

At pH values of 6.4 and above, the intensities within the high-energy region of the spectra (between 425 and 500 nm) increased nonlinearly when compared to the amounts of Co^{2+} detected on the surface. This behavior was inconsistent with that expected for increased loading of a 1:1 phen−Co surface adduct. Solution data for the phenanthroline complexes indicated that the spectra of the mono- and bis-complexes do not differ significantly in band shape, but the absorption intensity due to the bis-species is roughly 4-fold greater than that of the mono-species (SI Figure S7). In addition, the measured phen−Co ratio for the surface species in the pH region of 6.4−7.0 was increased relative to all other pH values, reaching a maximum ratio of 1.5:1 at pH 6.9. Taken together, these data are consistent with formation of a mixture of mono- and bis-species, although the measurements were not sufficiently precise to allow prediction of the exact fractional distribution of each. The data were therefore interpreted in terms of a model in which increasing amounts of $[Co(phen)_2]^{2+}$ began to bind to the surface as the pH was raised, most probably due to surface coordination via deprotonated $Si-O^-$ groups.

The diffuse reflectance spectra of $[Co(phen)]^{2+}$ samples showed increasing intensities in the region of 650 nm, characteristic of a tetrahedral species, when grafted at and above a pH value 6.4 (Figure 5). As the intensity of this spectral feature increased, the measured phen−Co ratio decreased, approaching the solution stoichiometry of 1:1. The diffuse reflectance spectra in the 575−700 nm range of the samples grafted at pH 8 and sample prepared later at pH 9.4 were very similar to that of the tetrahedral cobalt nitrate species and showed much less splitting of the spectral bands than was observed for the spectra of the DMP and MMP tetrahedral adducts. It thus appears that treatment of silica with a 1:1 mixture of Co^{2+} and phenanthroline at higher pH values affords mixtures of octahedral mono- and bisphenanthroline surface adducts, as well as tetrahedral adducts of unligated Co^{2+} ions.

The relative amount of mono- and bisphenanthroline complexes cannot be determined from the current data. Nevertheless, the binding and spectral data obtained in the pH range of 6.4−7.2 clearly shows a marked tendency for binding of the bisphenanthroline complex to the silica surface, affording materials with a ligand−Co ratio that significantly exceeds that of the grafting solution. We thus infer that there is a significant preference for coordination of the bisphenathroline complex to the silica surface. We considered the possibility that the driving force for formation of the mixed surface-bound species is provided by coordination of the unligated cobalt ion to the silica surface. This possibility was dismissed, however, on the grounds that binding of the phenanthroline complexes was detected at lower pH values than was binding of the unligated Co^{2+}. Such favorable binding of the bisphenanthroline complex is in accord with observations for the binding of the analogous copper bipyridyl complexes to silica surfaces.[26] We note that our data differ significantly from those reported by Park and Jung,[20] who showed a continuous decrease in ligand−Co ratios from a value of approximately 3.5 at pH 2 to approximately 1.5 at pH 7. We repeated our experiments using the phenanthroline assay as reported by those workers[20] and obtained essentially the same results as those described above. Although our procedures differ in some minor respects from those of Park and Jung,[20] we cannot identify a specific factor that would account for the differences in behavior that we have observed.

The pH titration data, diffuse reflectance spectra, and ratio of ligand−Co presented above for the MMP and phenanthroline adducts taken together indicated a complex model for the surface binding equilibria, contrasting starkly with the behavior of the more highly substituted DMP complex. The pertinent speciation behavior is summarized schematically in Figure 6. The complexity of the equilibria in such systems has been described before, particularly in the case of the metal−diimine complexes.[20,26,27] The data clearly indicate that steric factors have a strong influence on the surface binding preferences of the cobalt phenanthroline complexes. The unsubstituted phenanthroline complexes have a strong propensity to coordinate to silica as octahedral 2:1 phen−Co^{2+} species. This tendency is probably related to the stabilization of metal complexes having a combination of donor (i.e., silica) and acceptor (phenanthroline) ligands. Steric effects introduced by *o*-methyl substituents interfere

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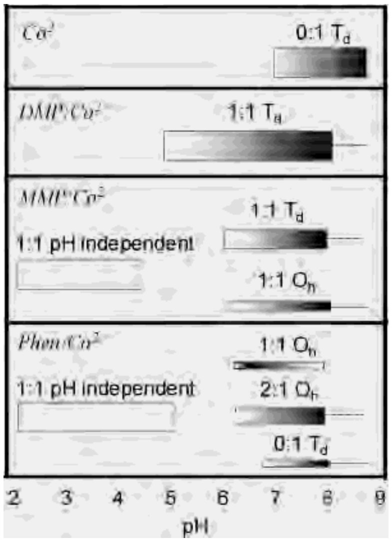

Figure 6. Schematic diagram representing the distribution of Co^{2+} species on the silica surface as a function of grafting pH and ligand steric bulk. Block thickness represents qualitatively the proportion of each species present. Gradients indicate increasing and decreasing concentration on the silica surface.

strongly with formation of the corresponding 2:1 MMP−Co^{2+} and DMP−Co^{2+} surface adducts. Consequently, the more sterically demanding ligands drive the complexes to form 1:1 surface adducts, which adopt tetrahedral geometries. Preferential formation of tetrahedral rather than octahedral surface adducts in the presence of the substituted ligands may simply reflect steric interactions at the silica surface, although entropic contributions from the release of two water molecules from the cobalt coordination sphere probably contribute to the formation of the tetrahedral geometry. In addition, when it is possible for only one acceptor ligand to be present, formation of the tetrahedral geometry may result in more favorable synergy between the donor and acceptor ligands.[26,28,29]

Conclusions

The binding of cobalt ions to silica surfaces in the presence of phenanthroline ligands substituted at the ortho- (2- and 9-) positions shows a clear dependence on ligand steric bulk. Whereas the unsubstituted phenanthroline promotes formation of an octahedral surface adduct with a 2:1 ligand−metal stoichiometry, the ortho-substituted MMP and DMP ligands induce a preference for binding as a tetrahedral adduct with a 1:1 ligand−Co^{2+} ratio. The initial objective of the study was to identify conditions under which octahedral surface adducts having a 1:1 diimine−metal ratio could be prepared. The creation of a homogeneous counterpart to the DMP adduct would permit a straightforward comparison of the influences of coordination geometry on catalytic activities. Since the unsubstituted phen ligand promoted formation of surface adducts with a different phen−Co^{2+} stoichiometry than those of the MMP and DMP ligands, such comparisons could not be accomplished using the current grafting procedure. Nevertheless, the data provide useful insight into the effects of ancillary ligands on coordination of metal ions at the silica surface. A clear understanding of such interfacial coordination effects will be important in designing hybrid materials for catalysis and other applications.

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Supporting Information Available: Plots of bound cobalt vs pH for Co^{2+}, MMP and phenanthroline complexes, reflectance spectra for Co^{2+} and $[Co(DMP)]^{2+}$ surface adducts, plot of bound Co^{2+} and L−Co^{2+} ratio for phenanthroline surface complex vs pH, and solution spectra for Co complexes with phenanthroline in PDF format. This information is available via the Internet at http://pubs.acs.org.

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