3954 *Inorg. Chem.* **1999,** *38,* 3954−3955

Effects of Multiple Covalent Attachments on Immobilized Iron(II)−1,10-Phenanthroline Complexes in Silica Sol−Gels

Grant M. Kloster, Colleen M. Taylor, and Stephen P. Watton*

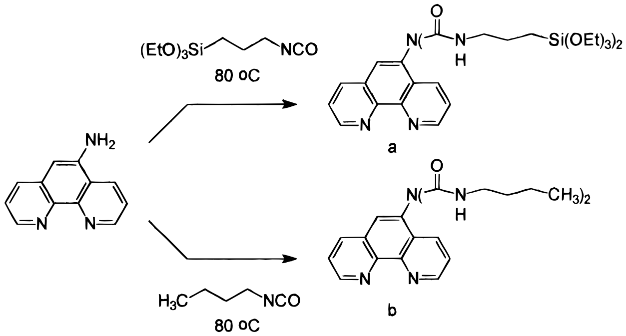
Department of Chemistry, Virginia Commonwealth University, 1001 West Main Street, P.O. Box 842006, Richmond, Virginia 23284

Received May 3, 1999

Immobilization of metal complexes in polymeric materials has emerged as a potential method for sequestering reactive species. The approach holds promise for the development of new heterogeneous catalysts,[1−7] sensors,[8,9] supramolecular devices,[10] and photonic devices.[11] A broad array of materials has been used to prepare supported reagents, including clay minerals,[12] zeolites,[13] alumina,[14] organic polymers,[1,2,15,16] and silica gels.[5,16−19] Silica sol−gels have the advantage that they can be prepared in optically transparent form, so that reactions occurring within the porous, solvent-filled interior[20] can be monitored by a variety of spectroscopic methods. Products and reactants are therefore readily characterized and quantified within the matrix.

Immobilized metal complexes doped into silica sol−gels must interact strongly with the matrix to hinder diffusion since the complexes can partition between the solid glass network and the pore solvent.[16,21] Inclusion of ligands bearing reactive alkoxysilyl side chains that copolymerize with the sol−gel precursor, $Si(OCH_3)_4$, ensures immobilization.[22] It has been established that covalent linking of metal complexes results in improved material integrity and catalytic behavior.[23] For example, carbonyl complexes of rhodium and cobalt with silylated phosphine ligands exhibit reduced leaching of metal ions and improved catalytic activities when attached to sol−gels.[17,24] Understanding the modified behavior of metal complexes immobilized in sol−gel matrices requires studying the molecular-level consequences of covalent attachment. We report here the effects of various numbers of covalent tethers on the stability of iron tris-phenanthroline complexes immobilized in silica sol−gels.

Scheme 1. Synthesis of Modified Phenanthrolines[a]



[a] (a) phen-Si. (b) phen-Bu.

A modified phenanthroline ligand suitable for tethering, phen-Si, was prepared by reacting 5-amino-1,10-phenanthroline with excess 3-(triethoxysilyl)propyl isocyanate (Scheme 1a).[25] A structurally analogous ligand, phen-Bu, which lacks the ability to form covalent tethers, was prepared similarly (Scheme 1b). Sol−gels were then prepared containing substituted ferrous tris-phenanthroline complexes in which the ratios of phen-Si to phen-Bu were varied systematically.[26] An excess of nickel(II) ions, which compete for the phenanthroline ligands,[27] was present in each sol to probe the influence of tethering on the complexes.[28] Reactions were monitored by observing the disappearance of the intense MLCT transitions of $[Fe(phen\text{-}Si)_m(phen\text{-}Bu)_{3-m}]^{2+}$ in the visible spectrum of each sol−gel. No further decrease in absorbance was observed after approximately 20 h, at which time the reactions were considered complete.

The tethers clearly stabilized $[Fe(phen\text{-}Si)_m(phen\text{-}Bu)_{3-m}]^{2+}$ ($m = 0-3$) toward competition by Ni^{2+} in the sol−gel as evidenced by retention of a significant fraction of the absorbance in all samples containing phen-Si ligands ($m > 0$). By contrast, almost complete loss of absorbance was observed for complexes which contained no tethers ($m = 0$). Furthermore, the extent of stabilization steadily increased with the fraction of tethered ligand

---

(1) Krebs, J. F.; Borovik, A. S. *J. Am. Chem. Soc.* **1995**, *117*, 10593−10594.
(2) Krebs, J. F.; Borovik, A. S. *Chem. Commun. (Cambridge)* **1998**, 553−554.
(3) Hartley, F. R. *Supported Metal Complexes*; Reidel: Dordrecht, 1985.
(4) Yermakov, Y. I.; Kuznetsov, B. N.; Zacharov, V. A. *Catalysis by Supported Complexes*; Elsevier: Amsterdam, 1981.
(5) Schubert, U.; Egger, C.; Rose, K.; Alt, C. *J. Mol. Catal.* **1989**, *55*, 330−9.
(6) Clark, J. H. *Catalysis of Organic Reactions by Supported Inorganic Reagents*; VCH: New York, 1994.
(7) Schubert, U.; Huesing, N.; Lorenz, A. *Chem. Mater.* **1995**, *7*, 2010−2027.
(8) Avnir, D. *Acc. Chem. Res.* **1995**, *28*, 328−334.
(9) Dave, B. C.; Dunn, B.; Valentine, J. S.; Zink, J. I. *Anal. Chem.* **1994**, *66*, 1120A−1127A.
(10) Greaves, M. D.; Rotello, V. M. *J. Am. Chem. Soc.* **1997**, *119*, 10569−10572.
(11) Castellano, F. N.; Meyer, G. J. *Prog. Inorg. Chem.* **1997**, *44*, 167−208.
(12) Laszlo, P. *Acc. Chem. Res.* **1986**, *19*, 121−127.
(13) Davis, M. *Acc. Chem. Res.* **1993**, *26*, 111−115.
(14) Posner, G. H. *Alumina and Alumina-Supported Reagents*; Laszlo, P., Ed.; Academic Press: New York, 1987; pp 287−315.
(15) Laszlo, P. *Preparative Chemistry Using Supported Reagents*; Academic Press: New York, 1987; Vol. VI.
(16) Adelt, M.; Devenney, M.; Meyer, T. J.; Thompson, D. W.; Treadway, J. A. *Inorg. Chem.* **1998**, *37*, 2616−2617.
(17) Schubert, U.; Rose, K.; Schmidt, H. *J. Non-Cryst. Solids* **1988**, *105*, 165−70.
(18) Schubert, U.; Breitscheidel, B.; Buhler, H. *Mater. Res. Soc. Symp. Proc.* **1992**, *271*, 621−32.
(19) Goersmann, C.; Schubert, U.; Leyrer, J.; Lox, E. *Mater. Res. Soc. Symp. Proc.* **1996**, *435*, 625−635.
(20) Dunn, B.; Zink, J. I. *Chem. Mater.* **1997**, *9*, 2280−2291.
(21) Castellano, F. N.; Heimer, T. A.; Tandhasseti, M. T.; Meyer, G. J. *Chem. Mater.* **1994**, *6*, 1041−1048.
(22) Noell, J. L. W.; Wilkes, G. L.; Mohanty, D. K.; McGrath, J. E. *J. Appl. Polym. Sci.* **1990**, *40*, 1177−1194.
(23) Deschler, U.; Kleinschmit, P.; Panster, P. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 236−252.
(24) Capka, M.; Schubert, U.; Heinrich, B.; Hjortkjaer, J. *Collect. Czech. Chem. Commun.* **1992**, *57*, 2615−2621.
(25) Elemental analysis data and integration of the ^1H NMR spectra for both phen-Si and phen-Bu indicated that the products were bis-ureylated.
(26) Sol−gels were prepared by addition of sol to premixed solutions containing aqueous $Fe(NH_4)_2(SO_4)_2$, and methanolic phen-Bu and phen-Si. The stoichiometries corresponded to a total of 3.1 equiv of phen-R to iron.
(27) Seiden, L.; Basolo, F.; Neumann, H. M. *J. Am. Chem. Soc.* **1959**, *81*, 3809−3813.
(28) The initial concentrations of reactants were 5 M $Si(OCH_3)_4$, 20 M H_2O, 0.8 M CH_3OH, 0.2 mM HCl, 2 mM $NiSO_4$, and 0.1 mM of the iron(II) phenanthroline complex under investigation.

10.1021/ic990471q CCC: $18.00

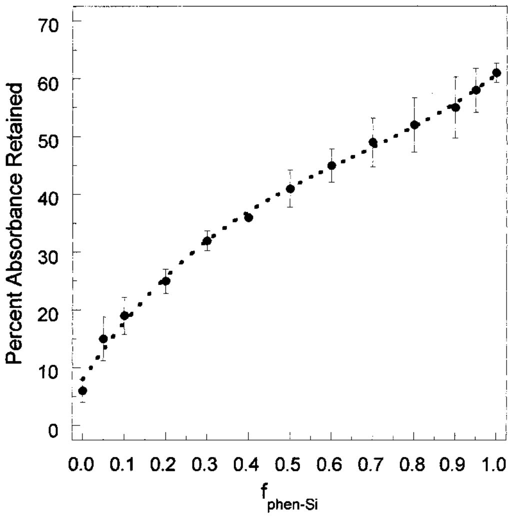


Figure 1. Percent absorbance retained versus fraction of tethered ligand, phen-Si, present in the solution used to prepare sols containing [Fe(phen-Si)$_m$(phen-Bu)$_{3-m}$]$^{2+}$. The starting absorbance for all of the metal complexes was approximately 1.28, corresponding to 0.1 mM solutions. The dotted line represents the curve obtained from the nonlinear least-squares fit of the data to eq 2 with %A_0 = 7.9, %A_1 = 45, %A_2 = 42, and %A_3 = 60.7. The error bars on the graph represent the standard deviation between three separate data sets.

(Figure 1). Comparable absorbance losses and reaction rates were observed for both [Fe(phen-Si)$_3$]$^{2+}$ and [Fe(phen-Bu)$_3$]$^{2+}$ in 80 mol % aqueous methanol solutions containing Ni^{2+}.[29] These control data verify that stabilization arises from tethering of the ligands to the silicate matrix, and that substituent effects on the kinetic and thermodynamic behavior are the same for both ligands in the absence of sol.[30]

The stabilization is not a monotonic function of the number of tethers, as illustrated by the sigmoidal curve in Figure 1. The absorbance data reflect ensemble behaviors that can be analyzed in terms of contributions from individual species. A ferrous solution containing two different substituted phenanthrolines with identical formation constants will have a statistical distribution of tris-chelate complexes with the formulas [Fe(phen-R)$_m$(phen-R′)$_{3-m}$]$^{2+}$ ($m = 0-3$, R = phen-Si, R′ = phen-Bu).[31] The fraction of each species present can be calculated as part of a binomial distribution with the expression

$$f_m = \left(\frac{3!}{m!(3-m)!}\right)(f_{\text{phen-Si}})^m(1 - f_{\text{phen-Si}})^{3-m} \qquad (1)$$

where f_m = the fraction of the species [Fe(phen-Si)$_m$(phen-Bu)$_{3-m}$]$^{2+}$ present in the final solution, $f_{\text{phen-Si}}$ = the fraction of phen-Si present in the phenanthroline mixture before iron is added, and m = 0, 1, 2, or 3.

The percentage of the initial absorbance retained, %A_{ret}, after a mixture of [Fe(phen-Si)$_m$(phen-Bu)$_{3-m}$]$^{2+}$ reacts with excess Ni^{2+} in the sol–gel can be described as a sum of the percentages of absorbance retained by each species, %A_m, multiplied by the fraction of each species initially present.

$$\%A_{\text{ret}} = \sum_{m}^{0-3} \%A_m f_m \qquad (2)$$

A nonlinear least-squares fit to the data in Figure 1 (dotted line) afforded values of %A_0 = 7.9 ± 0.9, %A_1 = 45 ± 2, %A_2 = 42 ± 2, and %A_3 = 60.7 ± 0.9.

A large excess of Ni^{2+} drives the substitution reactions to completion in aqueous methanol solutions. The residual absorbance, %A_0, for the untethered complex, [Fe(phen-Bu)$_3$]$^{2+}$, in Ni^{2+}-doped sol–gels indicates a small degree of partitioning of the complex between the silicate and bulk solvent[11] even in the absence of covalent attachments. Noncovalent association of molecules in sol–gels has been observed to influence the spectral,[20] photochemical,[11,16] and chemical[10] behavior of a variety of molecules.

The large increase in residual absorbance for the monotethered species, %A_1, presumably arises from increased steric hindrance, since the complexes are forced into proximity with the sol–gel matrix by the covalent attachment. The residual absorbance for the bis-tethered species, %A_2, is within error equal to %A_1, even though enhanced stability due to increased steric hindrance or macrochelate formation via the sol–gel framework might be expected. The apparent absence of macrochelate stabilization observed with two tethered ligands is readily explained if dissociation of the one untethered ligand from the Fe^{2+} center is sufficient to cause absorbance loss.[32] This argument is consistent with the behavior of the complexes having three covalently attached ligands, which show significantly enhanced stability as reflected by %A_3.[33]

In summary, covalent attachment both stabilizes and immobilizes iron phenanthroline complexes in sol–gels. Systematic variation of the ratio of tethered to untethered ligands indicated a general increase in stabilization with the number of tethers. Detailed statistical analysis revealed an unexpected similarity in stability between the complexes having one and two tethers. The behavior of complexes with successive numbers of tethers can be explained by a combination of steric and macrochelate effects, although other influences may contribute. The statistical analysis approach is being developed as a generalized tool for deconvoluting the behavior of mixed-ligand systems and is currently being used in our laboratory to study electron-transfer reactions and kinetic behavior in immobilization processes. Applications including the design and optimization of tunable catalysts, sensors, and devices are envisaged.

Acknowledgment. We thank the Jeffress Memorial Trust (Grant J-458) and Virginia Commonwealth University for funding this research. We also are grateful for helpful discussions with Professors Vincent Rotello and Caren Rotello.

IC990471Q

---

(29) Acidic conditions in sol–gels favor rapid hydrolysis of Si(OCH$_3$)$_4$ to Si(OH)$_4$ and CH$_3$OH followed by slower condensation to SiO$_2$. The initial sol thus comprised mostly acidic aqueous methanol (70–90 mol % CH$_3$OH); 80 mol % methanol was selected to mimic these conditions. See, for example: (a) Aelion, R.; Loebel, A.; Eirich, R. *J. Am. Chem. Soc.* **1950**, *72*, 5705–5712. (b) Iler, R. K. *The Chemistry of Silica*; John Wiley & Sons: New York, 1979. (c) Hench, L. L., West, J. K. *Chem. Rev.* **1990**, *90*, 33–72.

(30) Killingsworth, K. R.; Taylor, C. M.; Watton, S. P. Unpublished data.

(31) The concentrations of mono- and bis-phenanthroline ferrous complexes are negligible since the formation constants for these complexes are many orders of magnitude smaller than the formation constant for tris-phenanthroline iron(II). Irving, H.; Mellor, D. H. *J. Chem. Soc.* **1962**, 5222–5237.

(32) To our knowledge, the iron(II)–bis-phenanthroline complex has never been observed spectroscopically, due to the atypical relative magnitudes of the stepwise binding constants for mono-, bis-, and tris-iron(II) phenanthrolines (log K_1 = 5.1, log K_2 = 5.0, log K_3 = 10.0). The unusually large relative value of K_3 presumably reflects a transition from a high-spin to a low-spin configuration on binding of the third phenanthroline. The high-spin mono complex is essentially colorless, and it is reasonable to assume that the bis complex, also being high-spin, will exhibit similar spectral behavior. See citation in footnote 31.

(33) The tris-tethered complex presumably cannot lose any single phenanthroline through competition by Ni^{2+} due to the macrochelate effect. In this case, nickel substitution would be strongly disfavored since competition for the first phenanthroline, a necessary initial step in the overall substitution process, is thermodynamically uphill. See citation in footnote 31.