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# The Adsorption and Reaction of Coordination Complexes on Silica Gel

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Silica gel behaves as a weak acid ion exchanger. The negative surface sites are $\equiv$Si—O$^-$ and possibly $\equiv$Si(OH)$_2^-$. Adsorbed cations are weakly bound to surface sites and are readily exchangeable. Labile coordination complexes, for example nickel ammine complexes, readily interchange ammonia and water according to the concentration of ammonia in solution. Adsorbed inert complex cations which contain an aquo ligand react with surface silanol groups to bind $\equiv$Si—O$^-$ in the coordination sphere, and, in media of low dielectric constant, $\equiv$Si—O$^-$ can directly displace Cl$^-$ in adsorbed *trans*-Co(en)$_2$Cl$_2^+$. Species so bound are slowly extracted by dilute hydrochloric acid; nonbound inert complexes and labile complexes are extracted rapidly. We have determined the rates of hydrolysis of adsorbed *cis*-Co(en)$_2$NO$_2$Cl$^+$, *trans*-Co(en)$_2$Cl$_2^+$, Pt(dien)Br$^+$, and Si(acac)$_3^+$. The pH independent hydrolysis goes about one-fifth as fast as in bulk solution; the second-order hydrolysis goes much more slowly. Rates are first order at constant pH.

Representation of silica gel as a condensation polymer of silicic acid implies that the surface of silica gel is covered with –OH groups, silanol groups. Much evidence indicates that this is, indeed, the case. Various estimates of the number of such groups lie between 4.6[2a] and 8[2b] per 100 Å.$^2$ It is generally believed that the conventional silica xerogel is an agglomeration of spheroids, whose diameters are of the order of 100 Å., cemented by interparticle siloxane ($\equiv$Si—O—Si$\equiv$) links. The porosity and large surface area of silica gel, hundreds of square meters per gram, reflects this structure.

The surface silanol groups are strong hydrogen-bond donors,[3–5] and they rather strongly adsorb molecules containing groups which function as hydrogen-bond receptors. They are also weak acids. The p$K_a$ of the first ionization of free silicic acid is 9.9[6] and one would expect that of a surface silanol group to be fairly close to this.

It was observed long ago that cations could be adsorbed onto silica gel[7–11] by two methods. One can expose silica gel to a basic solution containing the cation, for example a solution of sodium hydroxide,[7] calcium hydroxide,[10] or an ammoniacal solution of copper hydroxide.[8–11] In the last case, the coordination complex, Cu(NH$_3$)$_4^{+2}$, which is adsorbed is not removed by washing with water,[10] but it is largely removed by washing with dilute acid.[12]

In the second method, one treats the gel with a dilute solution of sodium hydroxide and then washes it to near neutrality. Such gels adsorb cations from solution, presumably by ion exchange, since quantities of sodium ion equivalent to those of the ions adsorbed are liberated to the solution.[7] Ions such as Ag$^+$ and Cu$^{+2}$ (presumably hydrated) can be adsorbed by this method but not by the first method owing to the insolubility of the hydroxides.

Recent years have seen a considerable development of interest in this area.[13–19] It is the purpose of this article further to characterize the chemistry and mechanism of these cation adsorption phenomena.

## Experimental

**Silica Gels, Coordination Complexes.**—We have studied two types of silica gel: a conventional, rather narrow-pore material and a wide-pore gel; Davison Chemical Co. Grades 950 and 70, respectively. Among reported[20] impurities in the wide and narrow pore gels were: Na$_2$O, 0.062, 0.004%; CaO, 0.07, 0.018%; and Fe$_2$O$_3$, 0.010, 0.007%. The reported pore volumes were 1.16 and 0.4 cc./g.; the pore "diameters" were 140 and 25–27 Å.; and the surface areas were 340 and 600–700 m.$^2$/g. Unless otherwise stated, 40–60 mesh gel was used.

We are indebted to Prof. F. Basolo for many of the inert coordination complexes.

**Absorption Spectroscopy.**—Spectra of silica gels containing adsorbed ions were run on a Cary Model 14 by the following method. Silica gel was allowed to stand under carbon tetrachloride until air had been displaced from the pores of the gel. The wet gel was then added to a cuvette filled with carbon tetrachloride and this cell was used as a reference. Gel containing adsorbed ions was similarly put into the other cuvette. Fairly good spectra are obtained since the contents of the cuvettes are almost transparent.

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(2) (a) J. H. de Boer and J. M. Vleeskens, *Proc. Koninkl. Ned. Akad. Wetenschap.*, **B61**, 85 (1958); (b) C. C. Ballard, E. C. Broge, R. K. Iler, D. S. St. John, and J. R. McWhorter, *J. Phys. Chem.*, **65**, 20 (1961).

(3) R. K. Iler, "The Colloid Chemistry of Silica and Silicates," Cornell University Press, Ithaca, N. Y., 1955.

(4) A. V. Kiselev, "Second International Congress on Surface Activity," Academic Press, New York, N. Y., 1957, Vol. 2, p. 179.

(5) M. R. Basila, *J. Chem. Phys.*, **35**, 1151 (1961).

(6) S. A. Greenberg, *J. Am. Chem. Soc.*, **80**, 6508 (1958).

(7) W. A. Patrick and E. H. Barclay, *J. Phys. Chem.*, **29**, 1400 (1925).

(8) G. Testoni, *Ann. Chim. Applicata*, **16**, 45 (1926).

(9) R. Berthon, *Compt. rend.*, **195**, 43 (1932).

(10) I. M. Kolthoff and V. A. Stenger, *J. Phys. Chem.*, **38**, 475 (1934).

(11) G. W. Smith and L. H. Reyerson, *ibid.*, **38**, 133 (1934).

(12) L. H. Reyerson and R. E. Clark, *ibid.*, **40**, 1055 (1936).

(13) C. M. French and J. P. Howard, *Trans. Faraday Soc.*, **52**, 712 (1956).

(14) D. N. Strazhesko and G. F. Yankovskaya, *Ukrain. Khim. Zh.*, **25**, 471 (1959).

(15) H. W. Kohlschütter, *Chimia*, **14**, 285 (1960).

(16) S. Ahrland, I. Grenthe, and B. Norén, *Acta Chem. Scand.*, **14**, 1059 (1960).

(17) A. Kozawa, *J. Inorg. Nucl. Chem.*, **21**, 315 (1961).

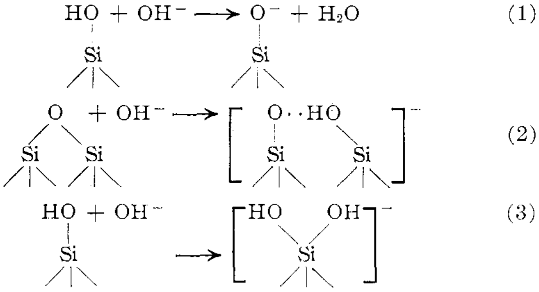
(18) D. L. Dugger, J. H. Stanton, B. N. Irby, B. L. McConnell, W. W. Cummings, and R. W. Maatman, *J. Phys. Chem.*, **68**, 757 (1964).

(19) (a) F. Vydra and V. Markova, *Talanta*, **11**, 433 (1964); (b) *J. Inorg. Nucl. Chem.*, **26**, 1319 (1964); (c) F. Vydra, *Talanta*, **10**, 753 (1963).

(20) From manufacturer's literature, but see (a) P. D. Klein, *Anal. Chem.*, **33**, 1737 (1961); (b) R. W. Dalton, J. L. McClanahan, and R. W. Maatman, *J. Colloid Sci.*, **17**, 207 (1962).

## Results and Discussion

Silica gel functions as a highly cross-linked weak acid ion exchanger.[21] Hydroxide ions react with the surface to form negative sites to which cations are bound. All of the following reactions are probably involved to some degree.



(1)

(2)

(3)

Surface silanol groups presumably condense to siloxane linkages until the strain becomes too great to permit further reaction. Repetition of reaction 2 is responsible for the solution of silica in aqueous base which begins at a pH of about 10.5.[22] Presumably, reaction 2 would occur more readily at strained siloxane linkages. Such strains should also favor formation of fivefold coordinated silicon by reaction 3. Stable five-coordinate species are known.[23] Reaction 2 should leave the siloxyl and silanol groups in a configuration suitable for hydrogen bonding and such configurations might also be present in reactions 1 and 3. Hydrogen bonding would increase the apparent acidity of the surface.[24]

If the ionization constant of a surface silanol group is about equal to the first ionization constant of silicic acid,[6] p$K_a$ for the first two reactions is 10 less any effect from hydrogen bonding, probably 1 or 2 p$K$ units. We have no way of estimating an equilibrium constant for reaction 3. We tentatively assume that reactions 1 and 2 are more important.

Consider silica gel partly in the sodium form suspended in water. A small amount of Na$^+$ diffuses into the water until the electric potential of the gel becomes negative enough to prevent further loss of Na$^+$. The negative potential in the gel tends to exclude OH$^-$ from the gel. At equilibrium, $a_\pm = \bar{a}_\pm$ where the bar over a species indicates the value in the interstices of the silica gel.[25] Let us consider a very simple model: swelling pressure negligible, activity coefficients equal unity, $K_w = \bar{K}_w$, and a uniform surface. Then from

$$m_{\mathrm{Na}^+}/\bar{m}_{\mathrm{Na}^+} = m_{\mathrm{H}^+}/\bar{m}_{\mathrm{H}^+} = \bar{m}_{\mathrm{OH}^-}/m_{\mathrm{OH}^-} \qquad (4)$$

the equation for electroneutrality in solution and in interstices, $K_w$, and

$$(\bar{m}_{\mathrm{R}^-})(\bar{m}_{\mathrm{H}^+}) = K_i\bar{m}_{\mathrm{RH}};\ \bar{m}_{\mathrm{R}^-} + \bar{m}_{\mathrm{RH}} = \bar{m}_{\mathrm{R}^0};\qquad f = \bar{m}_{\mathrm{R}^-}/m_{\mathrm{R}^0} \qquad (5)$$

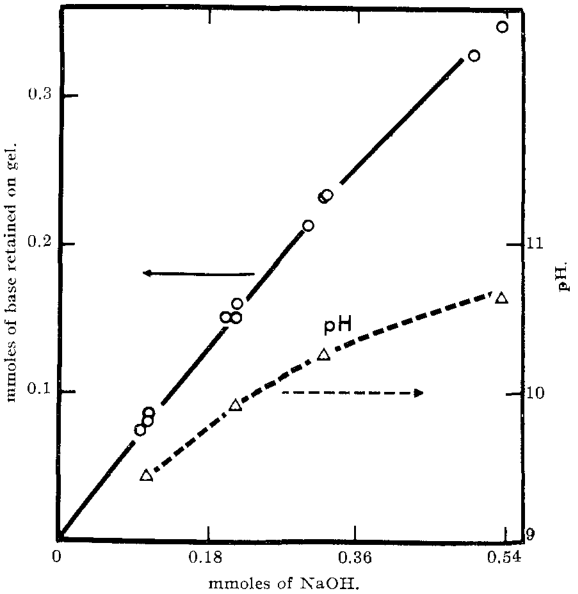


Figure 1.—Treatment of wide-pore silica gel with sodium hydroxide. Dashed line: pH of solution in 18 ml. of water of number of millimoles of sodium hydroxide shown on $x$ axis after stirring 0.5 hr. with 1 g. of gel. Full line: millimoles of sodium hydroxide retained by gels prepared as above after five washings with 10 ml. each of water.

where RH represents surface silanol groups, one gets

$$m_{\mathrm{H}^+} = K_i\,\frac{(1-f)}{f}\sqrt{\frac{1}{1+(K_i/K_w)(1-f)\bar{m}_{\mathrm{R}^0}}} \qquad (6)$$

For the wide-pore gel, if there are four surface silanol groups per 100 Å.$^2$, there are 2.3 moles of silanol groups per kg. In the 1160 g. of water which would fill the pores of the silica gel, $\bar{m}_{\mathrm{R}^0} = 2.3/1.16 = 2.0$. As long as $f$ is less than 0.5, the unity in the denominator of the expression at the right of eq. 6 is negligible and

$$m_{\mathrm{H}^+} = \frac{1-f}{f}\sqrt{\frac{K_wK_i}{\bar{m}_{\mathrm{R}^0}(1-f)}} \qquad (7)$$

On this model, if $f = 0.09$ and p$K_i = 8$, $m_{\mathrm{H}^+} = 0.7 \times 10^{-10}$, $m_{\mathrm{NaOH}} = 1.4 \times 10^{-4}$, and $\bar{m}_{\mathrm{OH}^-} = 1.1 \times 10^{-7}$.

In Figure 1 we show the results of adding dilute solutions of sodium hydroxide[26] to wide-pore gel which had been extracted with 0.1 $M$ hydrochloric acid and dried at 147° before use. The number of moles of sodium hydroxide shown on the $x$ axis was dissolved in 18 ml. of water and added to 1 g. of gel. The pH after stirring for 0.5 hr. is shown as the dashed line. The gel was then washed five times with 10 ml. of water and the amount of base still left on the gel was found by back titration of the washings. These values are shown as the full line. The per cent of base retained varied from 76% at the lowest concentration of sodium hydroxide to 65% at the highest. These retentions were confirmed by stirring the gel with an excess of 0.01 $M$ hydrochloric

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[21] F. Helfferich, "Ion Exchange," McGraw-Hill Book Co., New York, N. Y., 1962.

[22] Reference 3, p. 12.

[23] C. L. Frye, *J. Am. Chem. Soc.*, **86**, 3170 (1964).

[24] For a recent example of this effect see W. J. Middleton and R. V. Lindsey, Jr., *ibid.*, **86**, 4948 (1964).

[25] Reference 21, section 5-3, eq. 5-56.

[26] For other experiments on the reaction of sodium hydroxide with silica gel, see W. M. Heston, Jr., R. K. Iler, and G. W. Sears, Jr., *J. Phys. Chem.*, **64**, 147 (1960). The greater degree of reaction at a given pH with increasing concentrations of Na$^+$ in the aqueous phase is consistent with the Donnan equilibrium treatment given above.

acid for 5 min. and back titrating. In some runs, the acid extract was evaporated and the weight of the residue, taken as sodium chloride, was in agreement with hydrochloric acid consumption.

The wide-pore gel as supplied contains 0.056 mequiv./g. of basicity as determined by extraction with 0.01 *M* hydrochloric acid and back titrating and correcting for a loss of 0.007 mequiv. of acid when the operation is performed on gel which has been extracted with acid and dried at 147° before use. The sodium and calcium contents reported by the manufacturer correspond to 0.045 mequiv./g.

The sodium ions which are adsorbed on the gel are mobile even in the absence of added acid. Thus, a 40–60 mesh sample of wide-pore gel which had been extracted with acid and dried was treated with dilute sodium hydroxide and washed. The retained base was 0.24 mequiv./g. This and an equal quantity of base-free 12–20 mesh gel were stirred in water for 0.25 hr., the water was decanted, and the gel was spread on filter paper to remove free water. The gel was dried at 130° and reseparated into the different mesh sizes. The 12–20 mesh gel now contained 45% of the base.

The extractability of base by 0.01 *M* hydrochloric acid is little affected by drying the gel, although after drying at 147° the extraction may proceed a little more slowly.

**Exchange Capacity.**—The sodium ions present in the gel as supplied and those added by reactions 1, 2, or 3 are subject to ion exchange by other cations. Adsorption of cations from solutions containing ammonia may be considered to result from ion exchange with ammonium ions bound by reactions 1–3.

A rough measure of the exchange capacity of a base-treated gel is given by the width of the band which is formed when a known quantity of a colored ion in solution is passed through a column of the gel. We assume that 2 equiv. of sodium ion is liberated in the adsorption of doubly-charged ions, etc. The gels as supplied have exchange capacities of about 0.04 mequiv./g. Capacities of 0.16 mequiv./g. for the narrow-pore and 0.12 mequiv./g. for the wide-pore gel can readily be obtained by the methods used in Figure 1. These values were determined with tris(ethylenediamine)cobalt(III), $Co(en)_3{}^{+3}$, and bis(ethylenediamine)amminechlorocobalt(III), $Co(en)_2NH_3Cl^{+2}$. As the column is washed with water, the bands move through the column at a rate which is faster the less the charge on the adsorbed cation.[27]

Addition of ammonia to a pH of 9.5 provides an exchange capacity of wide-pore gel of 0.5 mequiv. with $Co(en)_2NH_3Cl^{+2}$.

Similar phenomena are exhibited in batch experiments. On base-pretreated wide-pore gel, anionic diamminetetranitrocobalt(III) is not adsorbed, and uncharged triamminetrinitrocobalt(III) is adsorbed slightly. Pentaamminenitrocobalt(III) is adsorbed to 0.013 mmole/g. at 0.0001 *M*, 0.028 mmole/g. at 0.0005 *M*, and 0.036 mmole/g. at 0.001 *M*. Tris(acetylacetonato)silicon (IV)is adsorbed less. Its adsorption seems to be linear to about a concentration of 0.001 *M* at which 0.02 mmole/g. is adsorbed.

**Adsorption and Reaction of Coordination Complexes.**—Adsorbed cations exhibit normal reactivities. Adsorption of nickel ion from the blue solution in dilute ammonium hydroxide gives a blue gel which changes to green upon washing with water and to magenta upon washing with concentrated ammonium hydroxide. These changes are reversible. Presumably the green gel is about the diammine; the blue, the tetraammine; and the magenta, the hexaammine. Dilute ethylenediamine changes the color to magenta. The color of this complex does not readily change on washing.

Similar behavior is exhibited by the adsorbed copper amine. As freshly prepared in excess ammonia the gel has the characteristic color of the tetraammine. Washing causes the color to become paler.[10] The air-dried material is even paler. Its absorption spectrum in carbon tetrachloride exhibits a maximum at 713 mμ suggestive of the monoammine.[28] Treatment with a dilute solution of ethylenediamine shifts the maximum to 563 mμ, indicative of adsorbed $Cu(en)_2.^{+2}$ Drying the gel at 175 or 560° shifts the maximum to beyond 800 mμ, suggestive of an ion coordinated to four oxygen atoms. This gel darkens upon treatment with dilute ammonia but not to the original color. However, dilute ethylenediamine gives $Cu(en)_2{}^{+2}$ and dilute potassium cyanide reacts rapidly to liberate cyanogen. A solution of potassium iodide reacts to liberate iodine but this reaction is slower.

Washing a gel containing adsorbed cations with 0.1 *M* hydrochloric acid reverses reactions 1 to 3 and liberates the cations. This requires about 15 sec. for the wide-pore gel and 2 min. for the narrow-pore. Presumably the rate is diffusion-controlled.

An inert complex containing an aquo ligand or a potential one adsorbed on silica gel exhibits a new phenomenon and constitutes an exception to the statement of the preceding paragraph. The complex reacts to bind a surface siloxy or silanol group into the coordination sphere. Studies with *trans*-bis(ethylenediamine)dichlorocobalt(III) chloride have been particularly revealing. Rapid hydrolysis of the complex in even slightly basic solution prevents adsorption by the ammonia method but adsorption on well-washed base-treated gel occurs without substantial hydrolysis. Subsequent reactions are shown in Figure 2.

The striking feature of Figure 2 is that species I is readily removed by dilute acid, like inert complexes in general, but that species II is not *displaced* by 0.1 *M* hydrochloric acid. The species slowly reacts with the acid to liberate $Co(en)_2ClH_2O^{+2}(aq)$, but the half-life of this reaction is several hours.

The pore water of a gel which has been treated with base, washed, saturated with *trans*-$Co(en)_2Cl_2{}^{+}$, and

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[27] In runs with 0.05 mmole of cation adsorbed on wide-pore gel and in which water was passed at 3.2 cc./min., the bands advanced a distance equal to their initial width with 2.4 l. of water for the doubly-charged ion and with 0.12 l. for a singly-charged ion ($Co(en)_2(NO_2)_2{}^{+}$). Even with 15 l., the band of the triply-charged species merely increased in width by 50%.

[28] J. Bjerrum, *J. Inorg. Nucl. Chem.*, **25**, 315 (1963).

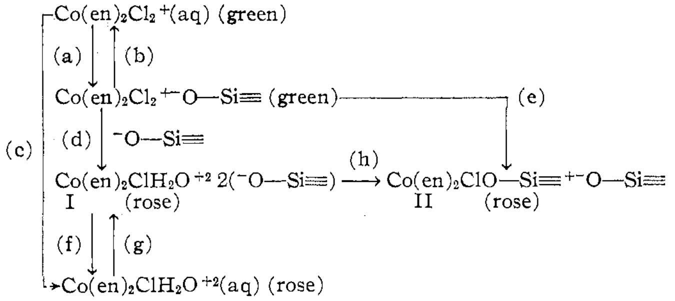

Figure 2.—Reactions of $Co(en)_2Cl_2{}^{+}$: (a) By reaction with base-treated wide-pore gel followed by washing with water. (b) Upon immediate extraction with 0.1 *M* HCl. (c) Upon standing in dilute solution overnight. (d) Immediately upon addition of a small amount of NaOH or $NH_3$(aq) to the water in contact with the gel. (e) Upon standing in water for 1.5 hr. and perhaps *via* I. (f) The complex is rapidly and nearly completely removed if the gel is extracted with 0.1 *M* HCl immediately after formation by steps (d) or (g). (g) Like (a). (h) Upon standing in water 1.5 hr.

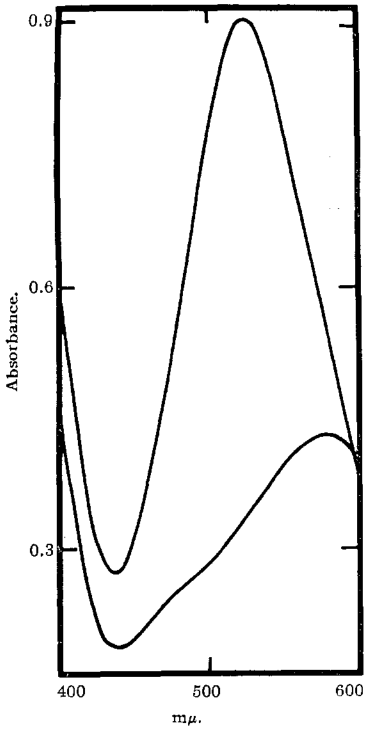

Figure 3.—Absorption spectra of coordination complexes on wide-pore silica gel. Upper curve: $Co(en)_2ClH_2O^{+2}$, mainly *cis*, adsorbed onto silica gel from solution. Lower curve: $Co(en)_2ClO\text{—}Si\equiv^{+}$, presumably mainly *trans*, prepared by reaction of adsorbed $Co(en)_2Cl_2{}^{+}$ on dried gel.

washed may be removed by washing with acetone and then chloroform or pentane. The gel so prepared reacts with a half-life of several hours if it is allowed to stand in the final solvent or if the solvent is poured off and the gel dried. The green gel becomes gray and then lavender. If, after 1 day, the gel is washed with water, a rose compound is removed which has the same spectrum as that of the solution at the bottom of Figure 2. Further extraction with 0.1 *M* hydrochloric acid removes nothing more immediately. The residual gel is grayish blue. It was washed with water, acetone, and carbon tetrachloride and its absorption spectrum run. The rose extract was adsorbed on base-treated silica gel and its absorption spectrum was also run. The spectra are given in Figure 3. If the gray-blue gel is allowed to stand in chloroform overnight, its color returns to lavender. Water extracts more of the rose complex and restores the color to grayish blue.

The absorption spectra of the complexes, in comparison with those of aqueous *cis*- and *trans*-$Co(en)_2H_2OCl^{+2}$,[29] suggest that the rose complex is mostly the *cis*-$Co(en)_2ClO\text{—}Si\equiv^{+}$ and that the lavender is largely the *trans* form. Thus, the following reactions occur and the first seems to be predominant.

$$\textit{trans}\text{-}Co(en)_2Cl_2{}^{+}{}^{-}O\text{—}Si\equiv \longrightarrow \textit{trans}\text{-}Co(en)_2ClO\text{—}Si\equiv{}^{+}Cl^{-} \quad (8)$$

$$\textit{trans}\text{-}Co(en)_2Cl_2{}^{+}{}^{-}O\text{—}Si\equiv + H_2O(ads) \longrightarrow \textit{cis}\text{-}Co(en)_2H_2OCl^{+2}{}^{-}O\text{—}Si\equiv Cl^{-} \quad (9)$$

The reaction of *cis*-$Co(en)_2H_2OCl^{+2}$ to form *cis*-$Co(en)_2ClO\text{—}Si\equiv^{+}$ may well involve addition of the oxygen attached to cobalt to silicon to form a five-coordinate intermediate. Thus, the oxygen atom in the Co–O–Si link may not have been exchanged. Further, judging from the colors of gel and extract, a little of step (e) in Figure 2 also involves reaction 8.

As suggested by reaction 8 silica gel covered with bound species become an anion exchanger. Thus, if a solution of *trans*-$Co(en)_2Cl_2{}^{+}$ is hydrolyzed to wine-red $Co(en)_2(H_2O)_2{}^{+3}$, adsorbed onto silica gel by the ammonia method, and allowed to stand overnight, little complex is removed by extraction with 0.02 *M* hydrochloric acid in a column. If the gel is washed with water until the concentration of chloride ion is low and then washed with dilute potassium nitrate, large quantities of chloride (as tested by $Ag^{+}$) appear in a sharp band.

*cis*-$Co(en)_2NO_2Cl^{+}$ and diethylenetriaminebromoplatinum(II) also become bound when these species adsorbed on silica gel are allowed to hydrolyze.

Just as on base-treated gel, cations adsorb on silica gel which has been treated with sodium fluoride and washed. The exchange capacity, however, seems to be smaller. The reactions described above for $Co(en)_2Cl_2{}^{+}$ adsorbed on base-treated gel also occur on complex adsorbed by the fluoride method. It is difficult to see how fluoride ion can be bound to the surface of silica gel except by a five-coordinate species analogous to that in reaction 3. Since fluoride ion and hydroxide ion have many characteristics in common, our assumption that reaction 3 is negligible may be incorrect. Further, reaction 8 and step (h) of Figure 2 may proceed with $\equiv SiOH$ as well as $\equiv SiO^{-}$.

**Rates of Hydrolysis.**—To this point we have not discussed the nature of cations adsorbed on silica gel. The assumption involved in eq. 4 that all activity coefficients are unity, although reasonable for the species in solution, may not be reasonable for adsorbed cations. As one approach to this problem we have determined the rates of hydrolysis of several adsorbed complex ions: *trans*-$Co(en)_2Cl_2{}^{+}$, *cis*-chloronitrobis-

[29] A. M. Sargeson, *Australian J. Chem.*, **16**, 352 (1963).

(ethylenediamine)cobalt(III) (*cis*-$Co(en)_2NO_2Cl^+$), bromodiethylenetriamineplatinum(II) ($Pt(dien)Br^+$), and tris(acetylacetonato)silicon(IV) ($Si(acac)_3^+$). A further interest in these experiments was the question as to whether reaction would involve water or $\equiv SiO^-$ as the substituting species. Also, we were interested in possible tests of reports that silica gel functions as a catalyst in certain reactions of coordination complexes.[30]

**Kinetic Runs.**—In runs with *cis*-$[Co(en)_2NO_2Cl]Cl$[31] and *trans*-$[Co(en)_2Cl_2]Cl$,[32] the complex dissolved in 100 ml. of water was added to 20 g. of silica gel which had been washed well with distilled water, treated with sodium hydroxide solution to a pH of 10, washed, and dried. No complex was visibly unadsorbed. With wide-pore silica gel 0.10 mmole of complex was used, with narrow-pore gel 0.25 mmole was used. The mixture was stirred in a thermostat at 25° and 5-ml. samples were removed periodically. Correction was made for the change in volume of the solution resulting from removal of the samples. In addition, with runs on the first complex, a number of check runs were made in which only one sample was removed and that at various times of reaction. Agreement was adequate.

In runs with $[Pt(dien)Br]Br$,[33] 0.408 mmole of complex in 100 ml. of water was added to 10.4 g. of base-treated gel and 5-ml. samples were removed. Here, 5 ml. of water returned after each aliquot to keep the volume constant. In runs with all three complexes, extent of reaction was determined by amperometric measurement of halide ion between a silver and a calomel electrode.[34]

Runs with $[Si(acac)_3]HCl_2$[35] were performed in two ways. In run I, 10 g. of base-treated silica gel was shaken with a solution containing the complex, the gel was washed with water for 25 min., and the volume was then brought to 220 ml. to start the run. About 0.2 mmole of $Si(acac)_3^+$ was found to have been present at the effective start of the run. In run II, this quantity of $Si(acac)_3^+$ was added to the same quantity of gel and water and the run was started. Samples of the aqueous phase were analyzed for $Si(acac)_3^+$ and acetylacetone spectrophotometrically at 2740 and 2890 Å. The rate of reaction of partial hydrolytic products is very fast so that only $Si(acac)_3^+$ and acetylacetone were observed. Not all of the complex was adsorbed. In run I after 5 min., the molar ratio of adsorbed complex to that in solution was about 10.5. In the first sample at 1.5 min., the ratio was 13. In the second run, the ratio increased from about 6 at 9 min. to 9 at 60 min. The adsorption of the $Si(acac)_3^+$ complex presents problems because the salt used forms $Si(acac)_3^+$, $2Cl^-$, and $H^+$ when dissolved in water. We used the excess base capacity of the base-treated gel to neutralize the excess acidity.

Buffer solutions were not employed in these runs despite the fact that acid is formed during the hydrolysis. The base-treated gel itself acts as a buffer. Since the base-treated, wide-pore gel contains the equivalent of about 0.2 mmole of base/g., much unexchanged base remained in all of our experiments. This provides rather good buffering action. The pH of the aqueous phase was measured periodically during the reaction. It rarely decreased by more than 0.2 unit during the entire period of observation.

Results of kinetic runs are presented in Table I. The "computed rate constant" is that for hydrolysis in homogeneous solution at the listed pH as computed from the literature. The listed pH is, of course, that of the solution in which the gel with adsorbed ion was immersed. The pH at the actual site of the adsorbed ions is unknown.

TABLE I

HYDROLYSES OF ADSORBED IONS AT 25°

| Adsorbed ion | Gel[a] | pH range | Av. pH[b] | Obsd. rate const. —sec.$^{-1}$ | Computed rate const.[c] × $10^5$— |
|---|---|---|---|---|---|
| *cis*-$Co(en)_2NO_2Cl^+$ | N.p. | 7.85–7.84 | 7.8 | 2.6 | 11 |
| | N.p. | 9.1–8.9 | 9.0 | 2.4 | 12 |
| | N.p. | 10.78–10.62 | 10.7 | 8.1 | 54 |
| | W.p. | 8.35–8.30 | 8.3 | 2.0 | 11 |
| | W.p. | 9.25–9.20 | 9.2 | 2.0 | 12 |
| *trans*-$Co(en)_2Cl_2^+$ | N.p. | 7.88–7.79 | 7.85 | 4.2 | 210 |
| | W.p. | 7.90–7.81 | 7.85 | 4.3 | 210 |
| $Pt(dien)Br^+$ | W.p. | | | 2.1 | 13 |
| $Si(acac)_3^+$ | W.p.[d] | 7.62–7.42 | 7.55 | 32 | 86 |
| | W.p.[e] | 7.10–6.63 | 6.95 | 22 | 42 |

[a] N.p. is narrow-pore, w.p. is wide-pore gel. [b] Average pH at time interval which determined the rate constant. [c] For *cis*-$Co(en)_2NO_2Cl^+$, $k = 11 \times 10^{-5} + 0.77C_{OH^-}$. For *trans*-$Co(en)_2Cl_2^+$, $k = 3.2 \times 10^{-5} + 3.0 \times 10^3 C_{OH^-}$. See ref. 30, Table 14. The hydrolysis of $Pt(dien)Br^+$ is pH-independent, $k = 13 \times 10^{-5}$, see H. B. Gray, *J. Am. Chem. Soc.*, **84**, 1548 (1962). For $Si(acac)_3^+$, $k = 2.6 \times 10^{-4} + 1.7 \times 10^3 C_{OH^-}$, see ref. 35. [d] Run I, see text. [e] Run II, see text.

**The State of the Adsorbed Cation.**—That all rate runs were first order in adsorbed ion demonstrates that the *average* environment of the adsorbed ion is independent of conversion. Since the data suggest that the adsorbed ions are neither really tightly bound nor free in the sense that $\gamma_{M^+}$ is near unity as assumed in eq. 4, the constancy of the average may well result from interchange of cations among a heterogeneous distribution of sites.

Rejection of really tight binding stems from the observation that adsorbed $Na^+$ equilibrates between different particles of gel (see just before Exchange Capacity) and from elution experiments.[27]

If $\gamma_{M^+}$ were near unity, eq. 4 and 6 would predict that $\bar{m}_{OH^-}$ (in the gel pores) would be about $0.001 m_{OH^-}$ (in the exterior solution). This factor should be reflected in the ratio of the rates of hydrolysis of *trans*-$Co(en)_2Cl_2^+$

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(30) F. Basolo and R. G. Pearson, "Mechanism of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1958, pp. 355–359.

(31) A. Werner, *Ann.*, **386**, 252 (1912).

(32) J. C. Bailar, Jr., *Inorg. Syn.*, **2**, 223 (1946).

(33) F. Basolo, H. B. Gray, and R. G. Pearson, *J. Am. Chem. Soc.*, **82**, 4200 (1960).

(34) I. M. Kolthoff and J. J. Lingane, "Polarography," Vol. 2, Interscience Publishers, New York, N. Y., 1952, part 6.

(35) R. G. Pearson, D. N. Edgington, and F. Basolo, *J. Am. Chem. Soc.*, **84**, 3233 (1962).

adsorbed and in solution since the rate of hydrolysis of this compound in solution is proportional to $m_{OH^-}$, the pH-independent contribution being negligible at these pH values. In fact, as shown in Table I, the ratio is 0.02. Any binding between cations and negative surface sites will decrease the degree to which hydroxide ions are excluded from the gel pores[36] and, therefore, will reduce the lowering of the observed rate constant.

Thus, the binding of the cation to the surface site must be moderate in strength. We cannot be more quantitative since the rate constant for the adsorbed ion could be affected by repulsion between $\equiv$Si—O$^-$ and OH$^-$ in any ion pair and by any alteration in the structure of water in the pores.

The pH-independent hydrolyses of $Co(en)_2NO_2Cl^+$ and $Pt(dien)Br^+$ go one-fifth as fast on silica gel as in solution. Thus, binding of these ions to negative surface sites does not greatly reduce the reactivity and we see no sign whatever that silica gel can catalyze solvolytic reactions.

The reduction in rate may result, in part, from shielding of bound cations by the surface and, in part, from a difference in structure between free water and pore water occasioned by hydrogen binding between surface silanol groups and water. Forslind[37] has suggested that such structural influences may extend 300 Å. from hydrophilic surfaces.

Several factors may be involved in cation binding. Most generally, electrostatic interaction will concentrate the cations at the walls in something like a diffuse double layer and may lead to ion pairing between surface siloxy anions and cations, particularly with multiply-charged cations.

Labile complexes may be bound by weak coordination of siloxy anions with ions which have square-planar coordination like Cu(II) or the siloxy anion may enter the coordination sphere of cations such as cupric and nickel. With inert complexes such substitution gives a surface compound, not an adsorbed ion.

Almost all of the complexes which we studied contained $RNH_2$ coordinated to a metal ion. Such somewhat acidic hydrogen atoms may hydrogen bond to $\equiv$Si—O$^-$.[38] The absence of such acidic hydrogen atoms in $Si(acac)_3^+$ may account for its reduced adsorption and increased rate of reaction relative to the other two pH-independent reactions of Table I.

Finally, any effect which increases the closeness of association between cation and $\equiv$Si—O$^-$ should increase the tendency for $\equiv$Si—O$^-$ to enter the coordination sphere directly as was indeed observed with $Co(en)_2Cl_2^+$ when water was replaced by a solvent of low dielectric constant or by air.

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(36) Reference 21, p. 137.

(37) E. Forslind, "Proceedings, Second International Congress on Rheology," Academic Press, New York, N. Y., 1954, p. 50.

(38) Such hydrogen bonding is not essential to adsorption since we find that both $Pd[((C_2H_5)_2NCH_2CH_2)_2NH]Cl^+$ and $Pd[((C_2H_5)_2NCH_2CH_2)NCH_3]Cl^+$ adsorb. See W. H. Baddley and F. Basolo, *J. Am. Chem. Soc.*, **86**, 2075 (1964).