is present as NO^-, and NO^- is a strong σ-donor ligand which competes favorably with NH_3 for σ electrons. This cobalt case is analogous to the situation in $[Cr(CN)_5NO]^{3-}$,[42] where the axial cyanide is more weakly bound than the equatorial cyanide. In the cobalt example, the two ligands are both competing for σ electrons, and NO^- is stronger than NH_3, while in the chromium case the two ligands are competing for π electrons, and NO^+ is apparently stronger than CN^-. In the present ruthenium case, however, the π-acceptor NO^+ ligand does not compete with the σ donor Cl^- ligand, and so both axial bonds (Ru–N and Ru–Cl) are strengthened.

This conclusion is supported by the structural data reported[33] for $[Ru(NO)(OH)(NO_2)_4]^{2+}$. Using Pauling's[43] value of 0.99 Å for the covalent radius of chlorine and our average equatorial Ru–Cl bond length of 2.376 Å we deduce an effective octahedral covalent radius for Ru(II) in these systems of 1.39 Å, which is in fair agreement with the value of 1.33 Å reported by Pauling.[43] A similar calculation, using the average Ru–NO_2 bond distance[33] in $[Ru(NO)(OH)(NO_2)_4]^{2+}$ of 2.079 Å and a covalent radius[43] for nitrogen of 0.70 Å, leads to a value of 1.38 Å. Using either of these two calculated radii and a covalent radius for oxygen of 0.66 Å,[43] one predicts that the Ru–O bond length should be approximately 2.04 Å. Hence, the axial Ru–O bond length[33] of 1.950 Å in $[Ru(NO)(OH)(NO_2)_4]^{2-}$ is much shorter than the calculated value; this is again a consequence of the successful competition of the σ-donor hydroxide ligand for σ electrons, in an exactly analogous manner to that found here for the axial Ru–Cl bond in $[Ru(NO)Cl_5]^{2-}$. We would anticipate similar results in other octahedral complexes in which one axial ligand is a π acceptor and the other is a σ donor.

The structural data are evidently in contradiction to the spectral data, which have been interpreted[14] as indicating that the axial Ru–Cl bond is weaker (and, presumably, longer) than the equatorial bonds. We assume that a reexamination of the spectral data, especially if Raman data become available to supplement the infrared data, will lead to the conclusion that the axial Ru–Cl bond is indeed stronger than the equatorial bonds.

Acknowledgments.—We are grateful to Professor E. E. Mercer for useful discussions concerning the spectra of this complex. This research was supported by the Advanced Research Projects Agency through Contract DAHC 15-67-C-0223 with the Materials Research Center of the University of North Carolina and by the National Science Foundation through Grant GP-10300; we gratefully acknowledge this financial support. J. T. V. thanks the Tennessee Eastman Corp. for a predoctoral fellowship.

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[43] L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960.

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Reaction of Catechol with Colloidal Silica and Silicic Acid in Aqueous Ammonia

BY DENNIS W. BARNUM

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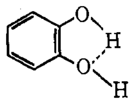
Reaction of catechol with silicic acid or colloidal silica in 8–15 *M* aqueous ammonium hydroxide gives large colorless crystals of a silicon–catechol complex that contains ammonia of crystallization. The ammonia can be removed at room temperature giving a product that analyzes for $(NH_4)_2[Si(C_6H_4O_2)_3]\cdot H_2O$. This compound has been studied by ir, nmr, X-ray powder diffraction, and its chemical behavior. The "water of crystallization" is probably present as an Si–OH group and a phenolic hydrogen. Removal of this "water" is difficult but can be accomplished in some cases. Other complexes have been prepared containing acetone, ethanol, dimethyl sulfoxide, or a fourth mole of catechol. A complex previously reported by other workers to contain 2 g-atoms of silicon/7 mol of catechol is actually the ethanol solvate $(NH_4)_2[Si(C_6H_4O_2)_3]\cdot xH_2O\cdot C_2H_5OH$ where x = 3 or 4.

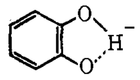
Introduction

Silicon forms very few coordination complexes with organic molecules and those that are known are generally unstable in the presence of water. An outstanding exception is catechol and other aromatic *vic*-diols which in aqueous basic solutions react with silica gel, colloidal silica, and even finely divided quartz to form coordination complexes of silicon.[1,2] Although these complexes have been investigated previously,[3–7] modern spectrometric methods have not been applied. In this investigation difficulty was encountered in repeating reported preparations and much of the previous work has been found to require modification.

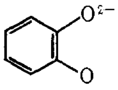
Rosenheim, *et al.*,[1] first reported the reaction of an aqueous solution of catechol with freshly precipitated silica in the presence of a base. They prepared $(NH_4)_2[Si(cat)_3]\cdot 9H_2O$[8] and several other salts of the $Si(cat)_3{}^{2-}$



H_2cat



$Hcat^-$



cat^{2-}

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[1] A. Rosenheim, B. Raibmann, and G. Schendel, *Z. Anorg. Chem.*, **196**, 160 (1931).

[2] A. Weiss, G. Reiff, and A. Weiss, *Z. Anorg. Allg. Chem.*, **311**, 151 (1961).

[3] A. Rosenheim and O. Sorge, *Ber.*, **53**, 932 (1920).

[4] H. Bartels and H. Erlenmeyer, *Helv. Chim. Acta*, **47**, 7 (1964).

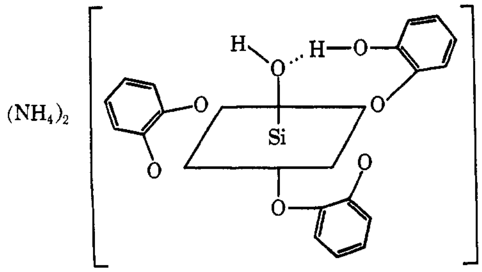
[5] H. Baumann, *Beitr. Silikose-Forsch.*, *Sonderb.*, **4**, 43 (1960).

[6] R. Hess, R. Bach, and H. Deuel, *Experientia*, **16**, 38 (1960).

[7] J. J. Flynn and F. Boer, *J. Amer. Chem. Soc.*, **91**, 5756 (1969).

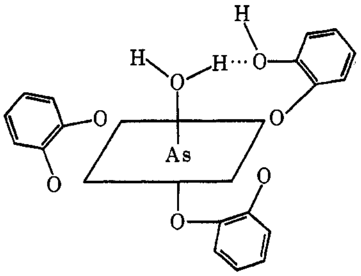
[8] It will be convenient in this paper to use the abbreviations H_2cat, $Hcat^-$, and cat^{2-} for catechol and its ions

ion. A simple octahedral structure was suggested in which the catechol ions are bidentate ligands. Weiss, *et al.*,[2] suggested a binuclear structure but recently Flynn and Boer[7] have determined the structure of the anhydrous pyridinium salt $(C_5H_6N)_2[Si(cat)_3]$ by X-ray diffraction and shown that it is mononuclear and has essentially the simple octahedral structure originally proposed by Rosenheim, *et al.* However, in a previous communication this author[9] suggested structure I for



I

those complexes containing "water of crystallization," including those prepared by Rosenheim and his coworkers. A similar structure, II, has been proposed



II

by Craddock and Jones[10] for the arsenic(V)–catechol complex $H[As(cat)_3]\cdot H_2O$.

Experimental Section

Preparation of the Ethoxy Derivative. $(NH_4)_2[Si(OC_2H_5)(Hcat)(cat)_2]$.—A successful preparation requires rigorous exclusion of water. All operations were carried out in a dry nitrogen atmosphere using a vacuum line and the anaerobic techniques reviewed by Herzog, Dehnert, and Lühder.[11] Ethanol was dried over calcium hydride and diethyl ether was dried over sodium. Both solvents were distilled as needed under dry nitrogen directly into the containers in which they were to be used. Glass containers were evacuated and heated with a heat gun before use in order to remove surface sorbed water.

A 250-ml three neck flask containing 5.28 g of catechol (48.0 mmol) was fitted with a reflux condenser and a gas inlet tube with a stopcock. The flask was evacuated and then filled with nitrogen. Fifty ml of diethyl ether was distilled into the catechol. Another 50 ml of ether was distilled into an addition funnel and to this was added 2.5 ml of silicon tetrachloride (22.0 mmol). The addition funnel was fitted onto the third neck of the reaction flask and, while passing a slow stream of nitrogen through the system, the silicon tetrachloride solution was slowly added to the catechol solution drop by drop. After addition was completed the solution was refluxed *gently* for 1 hr. The cooling water to the reflux condenser was turned off and the flow rate of nitrogen increased so that the ether distilled off. A viscous oil remained. The reflux condenser and addition funnel were replaced by stoppers and the remaining volatile material removed by vacuum. The vacuum must be applied slowly as serious foaming occurs. When foaming ceased and the pressure was less than 1 Torr the flask was heated on a steam bath for 30 min while pumping was continued. On cooling, the product was a hard resin with uncertain composition ($H_2[Si(cat)_3]$ or $ClSi(Hcat)_3$?).

This resin was dissolved in 50 ml of dry ethanol and anhydrous ammonia passed in while stirring on a magnetic stirrer. A white precipitate of $(NH_4)_2[Si(OC_2H_5)(Hcat)(cat)_2]$ formed (structure III) which was filtered off under nitrogen, washed with dry ethanol saturated with ammonia, and taken to constant weight under vacuum at room temperature. On contact with moist air it is rapidly converted to I.

The X-ray diffraction pattern[12] shows the three most intense lines at $d = 5.98$ Å (100), 5.64 Å (70), and 10.8 Å (55) (numbers in parentheses are relative intensities), as well as a line at $d = 2.74$ Å that is due to ammonium chloride impurity. If the analytical data are corrected for the presence of ammonium chloride the formula is $(NH_4)_2[Si(OC_2H_5)(Hcat)(cat)_2]$. *Anal.* Calcd for $(NH_4)_2[Si(OC_2H_5)(C_6H_5O_2)(C_6H_4O_2)_2]$: Si, 6.46; C, 55.27; H, 6.03; N, 6.45. Found: Si, 6.32, 6.28; C, 52.66; H, 6.38; N, 6.99; Cl, 1.92. Corrected for NH_4Cl: Si, 6.49; C, 54.23; H, 6.34; N, 6.42.

Preparation of $(NH_4)_2[Si(cat)_3]\cdot H_2O$. (a) From Silicic Acid.—This preparation must be carried out in the absence of air since alkaline solutions of catechol are rapidly oxidized by oxygen. Enough silicic acid to provide 26.6 mg-atoms of silicon and 10.0 g of catechol (91.0 mmole) were weighed into a 250-ml flask with a side arm and a straight bore stopcock. The exact weight of silicic acid required was determined from its water content and a finely ground product was used in order to ensure rapid reaction. The flask was stoppered, evacuated, and filled with nitrogen, and 75 ml of 15 *M* ammonium hydroxide was added by means of a hypodermic syringe with the needle inserted through the bore of the stopcock. The contents were stirred in order to dissolve all of the catechol. Reaction appeared to be complete after 2–8 hr but the mixture was allowed to stand overnight in order to ensure complete reaction. The crystalline product was filtered off under nitrogen, washed with cold 15 *M* ammonium hydroxide, and dried under vacuum at room temperature. Upon drying the crystals crumble to a white powder. The dry product was covered with ether and allowed to stand for 30 min in order to extract small amounts of catechol impurity. It was then filtered again, washed with ether, and dried to constant weight under vacuum at room temperature. The dry product can be handled in the open atmosphere without decomposition but it should be stored under nitrogen away from strong light. Because another complex containing 4 mol of catechol/g-atom of silicon sometimes coprecipitates, the X-ray diffraction pattern of each preparation should be examined for the absence of a line at $d = 9.1$ Å. The diffraction pattern has two intense lines at $d = 11.46$ Å (100) and 5.77 Å (95); all other lines have relative intensities less than 30. Analytical data are presented in Table I. If air has been carefully excluded during the preparation, I is a white powder.

(b) From Colloidal Silica.—Two different sources of commercial silica sol were used: Ludox, containing 735 mg of SiO_2/ml, from E. I. du Pont de Nemours and Co. and a sol containing 158 mg of SiO_2/ml from Dr. Theo. Schuchardt Gmb.H., Munich, West Germany.

The preparation used in this work was essentially the same as the preparation from silicic acid described above except that the reaction flask was first charged with 10.0 g of catechol (91.0 mmol), evacuated, and filled with nitrogen, and 100 ml of concentrated (15 *M*) ammonium hydroxide was added by means of a hypodermic syringe with the needle inserted through the bore of the stopcock. The proper volume of colloidal silica containing 26.6 mg-atoms of silicon and diluted to 20 ml was added in the same way and the mixture set aside overnight to react. The crystalline product was recovered and dried to constant weight as described above. The crystals crumble to a white powder on drying. The product was frequently contaminated with the complex containing 4 mol of catechol/g-atom of silicon.

The reaction was studied using different sources of silicon, different temperatures, various ratios of silicon to catechol, and various concentrations of ammonium hydroxide. As determined by X-ray diffraction patterns, numerous products were obtained,

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(9) D. W. Barnum, *Inorg. Chem.*, **9**, 1942 (1970).

(10) J. H. Craddock and M. M. Jones, *J. Amer. Chem. Soc.*, **83**, 2839 (1961).

(11) S. Herzog, J. Dehnert, and K. Lühder, "Technique of Inorganic Chemistry," Vol. VII, H. B. Jonassen and A. Weissberger, Ed., Interscience, New York, N. Y., 1968, pp 119–149.

(12) The X-ray powder diffraction patterns and complete tabulations of the lattice spacings and relative intensities have been deposited as Document No. NAPS-01648 with the ASIS National Auxiliary Publication Service, c/o CCM Information Corp., 909 3rd Ave., New York, N. Y. 10022. A copy may be secured by citing the document number and by remitting $2.00 for microfiche or $5.00 for photocopies. Advance payment is required. Make checks or money orders payable to: CCMIC–NAPS.

but when taken to constant weight the product was always I or a mixture of I and the catechol solvate. None of the intermediates was stable enough to isolate in a reliably pure form.

At room temperature the reaction with either silicic acid or colloidal silica in 15 M ammonium hydroxide gives some visible crystals after 5–30 min and reaction appears to be complete after approximately 8 hr. Colloidal silica reacts somewhat faster than silicic acid. In 10 M ammonium hydroxide several days is required for the reaction to go to completion. In 8 M ammonia the reaction is only partially complete after several weeks and in 6 M ammonia no crystalline product was obtained.

The above procedure gave the same product if run at either 5 or 40°. About a 20% excess of catechol is required to ensure that reaction with silica is complete. A larger excess of catechol is likely to cause formation of some of the catechol solvate $(NH_4)_2[Si(cat)_3]\cdot H_2O\cdot H_2cat$.

The composition of the crystals changes rapidly upon removal from the mother liquor. Analysis shows that they are losing ammonia. For example in one preparation the product was washed with acetone and ether and then dried 2 hr in a slow stream of dry ammonia gas. The container was then swept with dry nitrogen for 20 min to remove the gaseous ammonia. This product contained 11.0% N. After drying 48 hr in a slow stream of dry nitrogen it contained 7.16% N, after 96 hr, 6.40% N, and after 144 hr, 6.36% N. In other cases the crystals were dried in a slow stream of nitrogen which was then bubbled through 4% boric acid solution and finally after the crystals were at constant weight the ammonia was titrated with standard hydrochloric acid solution. Calculations of the amount of ammonia present in the original crystals gave values ranging from 2 to 4 mol of ammonia/g-atom of silicon.

(c) **From Silicon Tetrachloride.**—The preparation given above for the ethoxy compound $(NH_4)_2[Si(OC_2H_5)(Hcat)(cat)_2]$ was followed up to the formation of the resin. The resin was dissolved in absolute alcohol, and gaseous ammonia, saturated with water vapor by passing it through a tower of concentrated ammonium hydroxide, was introduced until no further precipitation occurred. Under these conditions the precipitate yields $(NH_4)_2[Si(cat)_3]\cdot H_2O$ upon drying to constant weight. The precipitate was filtered off under nitrogen, washed well with diethyl ether, and dried to constant weight under vacuum at room temperature.

(d) **Recrystallization of $(NH_4)_2[Si(cat)_3]\cdot H_2O$.**—This compound cannot be recrystallized from hot water because a precipitate of silica forms upon heating the aqueous solution.

Recrystallization was achieved by dissolving 4.3 g of I in 40 ml of 6 M ammonium hydroxide in a nitrogen atmosphere, filtering, and then passing in gaseous ammonia while cooling the solution to 0° in an ice bath. Colorless crystals of $(NH_4)_2[Si(cat)_3]\cdot xH_2O\cdot yNH_3$ formed, which were filtered off, washed with cold concentrated ammonium hydroxide, and dried to constant weight under vacuum at room temperature. Approximately 35% of the starting material was recovered.

(e) **Properties of $(NH_4)_2[Si(cat)_3]\cdot H_2O$.**—This compound is very soluble in water, dilute aqueous ammonia, ethanol and other alcohols, 2-ethoxyethanol, and dimethyl sulfoxide. It is insoluble in benzene, toluene, carbon tetrachloride, carbon disulfide, chloroform, dioxane, diethyl ether, acetonitrile, nitroethane, nitrobenzene, *N,N*-dimethylaniline, diethylamine, allyl chloride, and *tert*-butyl chloride. A small solubility was observed in tetrahydrothiophene 1,1-dioxide. In aqueous acid it immediately gives a precipitate of hydrated silica.

$(NH_4)_2[Si(cat)_3]\cdot 1.5H_2O$.—This compound was obtained on two occasions under quite different circumstances. No attempt was made to find a reproducible synthesis.

In the first case the procedure described above for the preparation of I from silicic acid was followed except that 12 M ammonium hydroxide was used for the reaction medium. The usual colorless crystalline product was obtained. After drying only 15 min under vacuum at room temperature most of the material still had the shape of the original crystals; only a small amount had disintegrated into a white powder. The product at this point gave an X-ray powder diffraction pattern with strongest lines at d (Å) = 10.8 (100), 7.5 (30), 7.0 (25), 6.65 (60), and 6.41 (25), and was stable on standing in air. However, upon taking this product to constant weight under vacuum the diffraction pattern changed to that of I.

In the second case, working under nitrogen, 2.0 g of I was dissolved in 22 ml of methanol (unknown water content), filtered, and set aside at −5°. Five days later colorless hexagonal crystals, 2–5 mm in diameter, were present. Upon drying 2 hr under vacuum at room temperature they disintegrated to a white powder and appeared to have reached constant weight. The X-ray diffraction pattern, however, showed it to be the sesquihydrate.

Anal. Calcd for $(NH_4)_2[Si(C_6H_4O_2)_3]\cdot 1.5H_2O$: Si, 6.76; C, 52.03; H, 5.58; N, 6.74. Found: Si, 6.70; C, 52.37; H, 5.66; N, 6.73.

Catechol of Crystallization—$(NH_4)_2[Si(cat)_3]\cdot H_2O\cdot H_2cat$. (a) From Silicic Acid.—The preparation was exactly the same as that of I described above, except that a large excess of catechol was used. Thus, 26.6 mg-atoms of silicon was taken, and 240 mmol (26.4 g) of catechol, which is 9 mol of catechol per g-atom of silicon. The reaction was carried out in 75 ml of 15 M ammonium hydroxide. A crystalline product was obtained in 10–30 min, but generally the mixture was allowed to stand overnight. The crystals were filtered off under nitrogen, washed with cold concentrated ammonium hydroxide, dried 2 hr under vacuum at room temperature, leached with ether, and dried to constant weight under vacuum at room temperature. The crystals crumble to a white powder on drying. The X-ray powder diffraction pattern generally shows some I as impurity.

(b) **From Silicon Tetrachloride.**—The preparation given above for the resin ($H_2[Si(cat)_3]$ or $ClSi(Hcat)_3$?) was followed. This resin was dissolved in 50 ml of dry ethanol and divided into two equal portions. To one portion gaseous ammonia saturated with water vapor was passed in which led to the preparation of I as described above. The second portion was held at 0° in an ice bath while passing in gaseous ammonia saturated with water vapor. A fine white precipitate formed which was filtered off, washed with cold ethanol saturated with ammonia, and dried 1 hr under vacuum at room temperature. The X-ray diffraction pattern of this product shows most intense lines at d (Å) = 10.5 (100), 10.0 (60), 9.2 (85), 5.8 (60), 4.35 (60), and 3.98 (40). It was not identified further. Upon standing in the open atmosphere for 2 days the diffraction pattern changed to that of $(NH_4)_2[Si(cat)_3]\cdot H_2O\cdot H_2cat$.

The product can be handled in the atmosphere once it is dry; however it discolors in a few days. It is best stored under nitrogen in the dark. The X-ray powder diffraction pattern has a single intense line at d = 9.1 Å. All other diffraction lines have relative intensities 25 or less.

Anal. Calcd for $(NH_4)_2[Si(C_6H_4O_2)_3]\cdot H_2O\cdot C_6H_6O_2$: Si, 5.44; C, 55.80; H, 5.46; N, 5.42. Found for three different preparations: Si, 5.49, 5.52, 5.41; C, 54.96, 54.84, 55.47; H, 5.58, 5.47, 5.76; N, 5.73, 5.84, 6.39.

Preparation of the Dimethyl Sulfoxide Solvate $(NH_4)_2[Si(cat)_3]\cdot H_2O\cdot 2CH_3SOCH_3$.—The following operations were carried out in the open atmosphere without noticeable decomposition. Dry reagent grade dimethyl sulfoxide (10 ml) was used to dissolve 1.0 g of I, and the resulting solution was filtered through highly retentive filter paper. While stirring, 25 ml of chloroform was added drop by drop. A precipitate formed after addition of about 10 ml of chloroform. It was filtered off, washed with chloroform, and dried under vacuum at room temperature to constant weight.

An ethanol solution of this compound was examined by tlc on alumina eluted with 90% toluene–10% ethanol. Two spots were observed; one with the same R_F as dimethyl sulfoxide, and one with the same R_F as I.

Anal. Calcd for $(NH_4)_2[Si(C_6H_4O_2)_3]\cdot H_2O\cdot 2(CH_3SOCH_3)$: Si, 4.99; C, 46.95; H, 6.09; N, 4.98; S, 11.39. Found for four separate preparations: Si, 5.49, 5.11, . . . , . . . ; C, 44.83, 45.35, 45.92, 46.95; H, 6.25, 6.22, 5.93, 5.85; N, 4.69, 4.75, 5.23, 5.15; S, 10.54, 10.79, 11.14, 11.39.

The X-ray powder diffraction pattern has several intense lines at d (Å) = 11.0 (95), 10.1 (35), 7.6 (40), 6.7 (35), 5.12 (30), 4.98 (100), 4.57 (50), 4.50 (30), 3.61 (45), and 3.50 (40). The infrared absorption spectrum is very similar to that of I except for bands at 9.9 and 10.5 μ that are due to the dimethyl sulfoxide. Crystals of a size suitable for X-ray diffraction studies can be grown by placing a solution of I in dimethyl sulfoxide inside a desiccator containing chloroform in the bottom. Isothermal distillation of chloroform into the dimethyl sulfoxide gradually occurs and crystals begin to form in about 10 days.

Preparation of the Ethanol Solvate $(NH_4)_2[Si(cat)_3]\cdot xH_2O\cdot C_2H_5OH$.—This product is obtained whenever $(NH_4)_2[Si(cat)_3]\cdot H_2O$ crystallizes from an aqueous ethanol solution. The procedure given above for the preparation of $(NH_4)_2[Si(cat)_3]\cdot H_2O$ from silicic acid was followed except that a mixture of 25 ml of

TABLE I

ANALYTICAL DATA FOR $(NH_4)_2[Si(cat)_3] \cdot H_2O$

		Prepn from $SiCl_4$		Prepn from	Prepn from silicic acid				
	Theory	Ref 3	This work	SiO_2 sol	This work				Ref 6
Si	6.91	7.04	6.86	6.81	7.01	6.93	6.98	6.92	7.10
C	53.18		52.83	52.39	53.04	52.95	52.01		54.69
H	5.46		5.40	5.56	5.49	5.32	5.49		5.40
N	6.89		6.73	6.48	6.58	6.15	6.67		6.93
O[a]	27.55		(28.2)	(28.8)	(27.9)	(28.6)	(28.8)		(25.88)
NH_4	8.88	8.88							

[a] Values for oxygen in parentheses are calculated by difference from 100%.

ethanol and 75 ml of 15 *M* ammonium hydroxide was used for the solvent. Three to five days at room temperature was required for the reaction to go to completion. The crystalline product was filtered off under nitrogen, washed with cold concentrated ammonium hydroxide, dried 5–10 min under vacuum, and finally dried to constant weight by standing over calcium sulfate in a desiccator filled with nitrogen. When dry it can be handled in the air without decomposition.

The nmr spectrum shows one ethyl group per three molecules of catechol with the methyl protons centered at τ 9.00 ppm and the methylene protons centered at τ 6.60 ppm relative to TMS. The X-ray powder diffraction pattern has most intense lines at d (Å) = 10.0 (100), 8.75 (30), 8.2 (20), 5.67 (25), 5.09 (25), 3.83 (50), and 3.15 (25).

The analytical data are not good enough to distinguish between 3 and 4 mol of water of crystallization. The best fit however is obtained assuming four "water" molecules. *Anal.* Calcd for $(NH_4)_2[Si(cat)_3] \cdot 4H_2O \cdot C_2H_5OH$: Si, 5.75; C, 49.16; H, 6.60; N, 5.73. Found: Si, 5.65, 5.77; C, 47.20; H, 6.59; N, 5.73.

On standing under vacuum this compound loses both water and ethanol, the final product being the "monohydrate," I. Large crystals (2.5 mm long) can stand in the open air for many days without noticeable decomposition and after 1 year in a closed vial were only partially converted to I. However, if ground to a fine powder it is completely converted to I by standing in air 2 days or by several hours under vacuum.

The ethanol solvate was also prepared on several occasions by adding ethanol to the filtrate obtained in the preparation of I from silicic acid or colloidal silica in concentrated ammonium hydroxide solution. About 50 ml of ethanol was added to the filtrate and the solution was stored overnight at 5°.

Also, the ethanol solvate can be prepared by dissolving 1.0 g of I in 30 ml of 50:50 ethanol–water (by volume) containing 1 ml of 15 *M* ammonium hydroxide and allowing this solution to stand overnight or longer at −5°.

Preparation of the Acetone Solvate $(NH_4)_2[Si(cat)_3] \cdot H_2O \cdot CH_3COCH_3$.—In some of the first preparations done in this work the crystalline products obtained in the reaction of silicic acid or colloidal silica with aqueous catechol were washed with acetone and then with ether. It was observed that more crystals form in the filtrate upon addition of the acetone. In three cases these crystals were also recovered, washed with acetone, and dried 1 hr under vacuum at room temperature. The X-ray powder diffraction pattern of the dried material has a single intense line at d = 10.7 Å (100). Of the remaining lines the more intense ones occur at d (Å) = 7.9 (12), 6.45 (14), 4.95 (25), and 3.35 (10). The ir spectrum shows only a weak band at 5.9 μ due to the C=O stretching band of acetone. The remainder of the ir spectrum is essentially the same as that of I.

Anal. Calcd for $(NH_4)_2[Si(cat)_3] \cdot H_2O \cdot CH_3COCH_3$: Si, 6.05; C, 54.29; H, 6.07; N, 6.03. Found for three different preparations: Si, 6.11, 5.99, 5.78; C, 52.74, 53.44, 54.56; H, 6.28, 6.02, 5.96; N, 6.27, 6.33, 5.86.

This compound was also obtained simply by covering I with acetone and allowing the mixture to stand for a few minutes. There is no visible change, but after such treatment the diffraction pattern is that of the acetone solvate. Acetone can be removed from the solvate simply by washing with ether. Obviously, acetone should not be used as a wash liquid; some of the diffraction patterns of early preparations of I in which this was done show the presence of acetone solvate as impurity.

Structure of $(NH_4)_2[Si(cat)_3] \cdot H_2O$

In this work all of the crystalline products obtained from the reaction of catechol with silica in aqueous ammonium hydroxide contained ammonia of crystallization and perhaps more than 1 mol of water of crystallization. They begin to lose ammonia as soon as they are removed from the mother liquor so it was not possible to establish an exact composition. The general formula, however, is $(NH_4)_2[Si(cat)_3] \cdot xH_2O \cdot yNH_3$, where x = 1 or 2 and y = 2–4. Other catechol complexes containing ammonia of crystallization have been reported previously, namely, $R_2[Ti(cat)_3] \cdot 5NH_3$[13] and $H[As(cat)_3] \cdot H_2O \cdot {}^7/_3NH_3$.[14] It is likely that different amounts of water and ammonia are obtained depending on the conditions of the reaction. Many different X-ray powder diffraction patterns were obtained but no reproducible behavior was evident. The diffraction patterns are complex, containing many lines, and appear to depend on the concentration of ammonia in the solution from which the crystals formed as well as the drying time. Nevertheless, all of these products gave the diffraction pattern of $(NH_4)_2[Si(cat)_3] \cdot H_2O$ after taking to constant weight (although sometimes the catechol solvate $(NH_4)_2[Si(cat)_3] \cdot H_2O \cdot H_2cat$ was present as an impurity).[15] Almost identical behavior has been observed in the reaction of catechol with niobium and tantalum hydroxides.[16]

Analytical data for several preparations of $(NH_4)_2[Si(cat)_3] \cdot H_2O$ from silicic acid, colloidal silica, and silicon tetrachloride are given in Table I. The data agree best with a complex containing 1 mol of water of hydration. Previous data on the amount of water are conflicting. Rosenheim and Sorge[3] found 9 mol of water and Weiss, *et al.*,[2] found 4.5 but neither of these groups dried their product to constant weight nor did they report ammonia of crystallization in their products. Hess, *et al.*,[6] found 1 or 2 mol of water. Weiss, *et al.*, found that the silicon and germanium complexes are isomorphous. Unfortunately they gave no analytical data for their germanium complex, but Bevillard[17] found $(NH_4)_2[Ge(cat)_3] \cdot 1.5H_2O$. A silicon complex with 1.5 mol of water was also isolated in this work and, as shown by its X-ray diffraction pattern, is definitely different from the monohydrate.

Rosenheim and Sorge[3] claimed to have prepared anhydrous $(NH_4)_2[Si(cat)_3]$ from the reaction of catechol with silicon tetrachloride. Since their preparation was supposedly done in the absence of water, it is not surprising that they did not consider the possibility of a hydrate. However, in this work it was found that one must exclude water rigorously if the monohydrate is to be avoided, and even then the product is $(NH_4)_2$[Si-

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[13] C. Gopinathan and J. Gupta, *Indian J. Chem.*, **3**, 470 (1965).

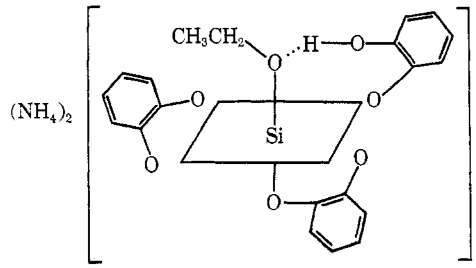
[14] R. F. Weinland and J. Heinzler, *Ber.*, **52**, 1316 (1919).

[15] The ir spectra cannot be used to distinguish the various products as the differences are too slight and occur mainly in the N–H and O–H stretching region where there is a great deal of overlapping.

[16] F. Fairbrother, N. Ahmed, K. Edgar, and A. Thompson, *J. Less-Common Metals*, **4**, 466 (1962).

[17] P. Bevillard, *Bull. Soc. Chim. Fr.*, 296 (1954).

$(OC_2H_5)(Hcat)(cat)_2]$ (structure III). Upon contact with moist air the ethoxy compound is converted within 30 min into the monohydrate, I. Since Rosenheim and Sorge did not mention any special precautions to avoid contact with water and since their analytical data are in better agreement with a monohydrate than an anhydrous complex (see Table I), it is probable that they had, in fact, prepared the monohydrate.



III

Flynn and Boer[7] have established the structure of the anhydrous pyridinium salt $(C_5H_6N)_2[Si(cat)_3]$ by an X-ray diffraction study of a single crystal, and in this laboratory it has been found that the water can be removed from $Mg[Si(cat)_3]\cdot H_2O$ by heating at 100° under vacuum for 166 hr. In a previous communication[9] structure I was proposed for the "monohydrate." One would tend to question this formulation in view of the X-ray structure determination on the pyridinium salt; however, the evidence for structure I is strong and it still deserves serious consideration for those compounds containing "water of crystallization."

The main evidence for structure I was obtained from the reaction of silicon tetrachloride with catechol in anhydrous ether. The hydrogen chloride that was produced by the reaction, as well as the ether, was removed by sweeping with nitrogen and finally by vacuum. A resinous product remained which had an uncertain composition. Weiss, *et al.*,[2] and Schwarz and Kuchen[18] claimed it to be $H_2[Si(cat)_3]$ but Rosenheim and Sorge[3] claimed it to be $ClSi(Hcat)_3$. None of these workers presented convincing data and work in this laboratory so far has given conflicting results. If gaseous ammonia is passed into a solution of this resin in anhydrous ethanol, an ammonium salt precipitates which contains an ethyl group and probably has structure III. It is especially sensitive to moisture and is completely converted to I on contact with the open atmosphere for 30 min.

The water in $(NH_4)_2[Si(cat)_3]\cdot H_2O$ is much more strongly held than one would expect for simple water of crystallization. Thus, heating under vacuum (<1 Torr) for 2 weeks at 60° resulted in discoloration, but the X-ray diffraction pattern remained unchanged. Similar behavior has been observed by other workers in other catechol complexes. Reihlen, Sapper, and Kall[19] reviewed the early data available and concluded that 1 mol of water in $K[Sb(cat)_3]\cdot 1.5H_2O$, $H[As(cat)_3]\cdot H_2O$, and $K_3[Fe(cat)_3]\cdot H_2O$ is coordinated to the metal rather than being present as simple water of crystallization. Rosenheim, *et al.*,[1] also noticed a particularly strong tendency for complexes of $Ti(cat)_3{}^{2-}$ to retain at least 1 mol of water. Fairbrother, *et al.*,[16] suggested $(NH_4)_3[Nb(OH)_2(cat)_3]\cdot H_2O$ as a possible formulation of a niobium–catechol complex and Craddock and Jones[10] favored structure II for the arsenic complex. Finally, "chelation" by a hydrogen bond as in structures I–III has been established in a nickel(II)–catechol complex by an X-ray diffraction structure determination.[20]

The water in $(NH_4)_2[Si(cat)_3]\cdot H_2O$ is probably present as an Si–OH group and a phenolic hydrogen rather than an $Si–OH_2$ group. Since the acidity of water is enhanced by coordination to a metal and the phenoxide ion is a strong base, one would expect the following equilibrium to lie far to the right

$$\text{Si–OH}_2 + \text{Ar–O}^- = \text{Ar–OH} + \text{Si–OH}$$

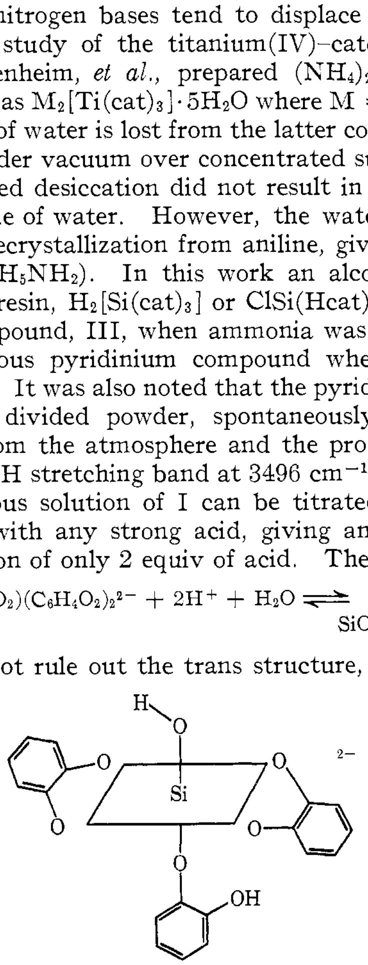
The infrared absorption spectrum of $(NH_4)_2[Si(cat)_3]\cdot H_2O$ shows a sharp band at 3545 cm^{-1} which is characteristic of free or weakly associated –OH groups. Pauling[21] investigated the near-infrared (overtone region) spectrum of catechol and found two –OH bands: one at 6970 cm^{-1} which he assigned to the hydrogen-bonded O–H···O group and one at 7060 cm^{-1} due to the free –OH group. The 7060-cm^{-1} overtone corresponds to a fundamental at 3530 cm^{-1} which is close to the 3545-cm^{-1} band observed in the silicon complex. Structure I also contains a hydrogen-bonded –OH group but this region of the spectrum is obscured by the N–H bands of the ammonium ions.

With respect to the difference between $(NH_4)_2[Si(cat)_3]\cdot H_2O$ and the anhydrous pyridinium salt it appears that nitrogen bases tend to displace the water. Thus, in a study of the titanium(IV)–catechol complexes, Rosenheim, *et al.*, prepared $(NH_4)_2[Ti(cat)_3]\cdot H_2O$ as well as $M_2[Ti(cat)_3]\cdot 5H_2O$ where M = K or Rb. Four moles of water is lost from the latter complexes on standing under vacuum over concentrated sulfuric acid but prolonged desiccation did not result in the loss of the last mole of water. However, the water was displaced by recrystallization from aniline, giving $M_2[Ti(cat)_3]\cdot 4(C_6H_5NH_2)$. In this work an alcoholic solution of the resin, $H_2[Si(cat)_3]$ or $ClSi(Hcat)_3$, gave the ethoxy compound, III, when ammonia was added but the anhydrous pyridinium compound when pyridine was added. It was also noted that the pyridinium salt, if a finely divided powder, spontaneously picks up moisture from the atmosphere and the product shows a sharp –O–H stretching band at 3496 cm^{-1}.

An aqueous solution of I can be titrated potentiometrically with any strong acid, giving an end point after addition of only 2 equiv of acid. The reaction is

$$Si(OH)(C_6H_5O_2)(C_6H_4O_2)_2{}^{2-} + 2H^+ + H_2O \rightleftharpoons SiO_2 + 3C_6H_6O_2$$

One cannot rule out the trans structure, IV, on the



IV

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[18] R. Schwarz and W. Kuchen, *Z. Anorg. Allg. Chem.*, **266**, 185 (1951).

[19] H. Reihlen, A. Sapper, and G. A. Kall, *ibid.*, **144**, 218 (1925).

[20] L. Sacconi, P. L. Orioli, and M. DiVaira, *Chem. Commun.*, 849 (1967).

[21] L. Pauling, *J. Amer. Chem. Soc.*, **58**, 94 (1936).

basis of the available data, but the extra stability of the hydrogen bond would tend to favor I and one might expect that the phenolic -OH group in IV could be titrated in nonaqueous media. In fact, titration in anhydrous isopropyl alcohol with KOH in isopropyl alcohol failed to give any inflection. Also, the arsenic complex, II, which behaves very much like I, has been resolved into an optically active enantiomorph. This rules out a structure analogous to IV for the $[\mathrm{As(OH)(Hcat)(cat)_2}]^-$ ion.

Solvates of $(\mathrm{NH_4})_2[\mathrm{Si(cat)_3}]\cdot\mathrm{H_2O}$

Weiss, *et al.*,[2] reported isolating a complex containing 7 mol of catechol/2 g-atoms of silicon which they formulated as $(\mathrm{NH_4})_4[\mathrm{Si_2(cat)_5(Hcat)_2}]\cdot 9\mathrm{H_2O}$. They prepared the compound by adding ethanol to the filtrate obtained from the preparation of $(\mathrm{NH_4})_4[\mathrm{Si_2(cat)_6}]\cdot 9\mathrm{H_2O}$. Their synthesis was repeated in this work but it was found that the compound is really an ethanol solvate and should be formulated as $(\mathrm{NH_4})_2[\mathrm{Si(cat)_3}]\cdot x\mathrm{H_2O}\cdot\mathrm{C_2H_5OH}$ where $x = 3$ or 4. The nmr spectrum in deuterated DMSO shows one ethyl group for every three catechol groups.

Besides the ethanol solvate, compounds were obtained containing catechol, dimethyl sulfoxide, and acetone: $(\mathrm{NH_4})_2[\mathrm{Si(cat)_3}]\cdot\mathrm{H_2O}\cdot\mathrm{H_2cat}$, $(\mathrm{NH_4})_2[\mathrm{Si(cat)_3}]\cdot\mathrm{H_2O}\cdot 2\mathrm{CH_3SOCH_3}$, and $(\mathrm{NH_4})_2[\mathrm{Si(cat)_3}]\cdot\mathrm{H_2O}\cdot\mathrm{CH_3COCH_3}$. All have 1 mol of water, which supports the thesis that the water is an intimate part of the complex rather than simple water of crystallization.

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Notes

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The Preparation of σ-Bonded Platinum Complexes of Methylcarborane(12)

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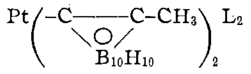
Reports of π-bonded transition metal complexes with $\mathrm{B_9C_2H_{11}}^{2-}$, $\mathrm{B_7C_2H_9}^{2-}$, and $\mathrm{B_6C_2H_8}^{2-}$ ligands are numerous.[1] A few examples of neutral σ-bonded transition metal complexes involving single carbon-transition metal bonds have appeared in the literature. In this paper we report a number of σ-bonded phosphinoplatinum complexes of $1\text{-}\mathrm{CH_3}\text{-}1,2\text{-}\mathrm{B_{10}C_2H_{11}}$ of the type



$$\mathrm{Pt}\left(-\underset{\substack{\diagdown\mathrm{O}\diagup\\ \mathrm{B_{10}H_{10}}}}{\mathrm{C}\text{——}\mathrm{C}}-\mathrm{CH_3}\right)_2\mathrm{L_2}$$

When L is $\mathrm{P(C_6H_5)_3}$, $\mathrm{P(CH_3)(C_6H_5)_2}$, $\mathrm{P(CH_3)_2(C_6H_5)}$, or $\mathrm{P(CH_3)_3}$, cis complexes were obtained. When the L is $\mathrm{P}(n\text{-}\mathrm{C_4H_9})_3$, a trans complex is obtained. We suggest a reason that the cis complex of $\mathrm{P}(n\text{-}\mathrm{C_4H_9})_3$ could not be obtained.

Experimental Section

General Techniques.—A Perkin-Elmer 457 grating spectrophotometer was used to obtain the infrared spectra. Solid spectra were run either as Nujol or as Fluorolube mulls between CsI plates.

Proton nmr spectra were observed by means of a Varian Model 56/60 nuclear magnetic resonance spectrometer operating at the ambient temperature of the instrument. Tetramethylsilane was employed as internal standard. Phosphorus and boron nmr absorptions were obtained on an NMR Specialties MP1000 pulsed spectrometer with an operating frequency of 65 MHz and a field strength of 47.6 and 28.0 kG, respectively. Solutions of $\mathrm{P_4O_6}$ and $\mathrm{B(OCH_3)_3}$ were employed as internal references, by the capillary insertion technique.

Mass spectral data were obtained by means of a Hitachi-RMU-6 spectrometer operating with an ionizing voltage of 56 V.

The preparations were carried out under an atmosphere of dry nitrogen. Analyses were performed by Spang Laboratories, Ann Arbor, Mich., or by Chemalytics, Inc., Tempe, Ariz. Melting points were obtained by the use of a Thomas-Hoover capillary melting point apparatus.

Methylcarborane [1-Methyl-1,2-dicarba-*closo*-dodecaborane-(12)].—This was prepared from purified propargyl bromide (3-bromopropyne), acetonitrile, and decarborane (U. S. Air Force) by the use of a method previously described.[3] The identity of the product was established by its melting point (211 ± 2°, lit.[3] mp 211-213°) and by a comparison of the ^{1}H nmr with the reported values. The ^{1}H nmr spectrum ($\mathrm{CS_2}$) exhibited absorptions at δ 3.50 (broad singlet, intensity 1, due to the C-H on methylcarborane(12)), and δ 2.00 (broad singlet, intensity 3, due to the *C*-methyl protons) (lit.[3] δ 3.48 and 1.48, respectively). The pure methylcarborane(12) was stored in an evacuated desiccator over $\mathrm{P_2O_5}$ prior to use.

Synthesis of the Cis Platinum-Phosphine Complexes.—The following platinum compounds *cis*-dichlorobis(trimethylphosphine)platinum(II) [*cis*-$\mathrm{PtCl_2[P(CH_3)_3]_2}$], *cis*-dichlorobis[di-

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[1] M. F. Hawthorne, D. C. Young, T. D. Andrews, D. V. Howe, R. L. Pilling, A. D. Pitts, M. Reintjes, L. F. Warren, Jr., and P. A. Wegner, *J. Amer. Chem. Soc.*, **90**, 879 (1968); M. F. Hawthorne and T. A. George, *ibid.*, **89**, 7114 (1967); T. A. George and M. F. Hawthorne, *ibid.*, **90**, 1661 (1968); G. Popp and M. F. Hawthorne, *ibid.*, **90**, 6553 (1968); M. F. Hawthorne and H. R. Ruhle, *Inorg. Chem.*, **8**, 176 (1969); T. A. George and M. F. Hawthorne, *J. Amer. Chem. Soc.*, **91**, 5475 (1969); M. F. Hawthorne, *Accounts Chem. Res.*, **1**, 281 (1968).

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