**Table I.** First-Order Rate Constants for the Aquation of $Cr(H_2O)_5(3\text{-pic})^{3+}$ at $1.0\,M$ Ionic Strength $(HClO_4 + NaClO_4)^a$

Temp, °C	$(HClO_4)$, mM	$10^4 k_{obsd}$, sec^{-1}	Temp, °C	$(HClO_4)$, mM	$10^4 k_{obsd}$, sec^{-1}
99.0	1000	1.08	85.0	99.6	0.407
99.0	100	2.38	85.0	14.1	1.65
99.0	24.4	6.19	85.0	5.91	3.55
99.0	14.3	9.79	85.0	2.76	7.17
99.0	8.28	15.4	80.0	14.3	0.781
99.0	6.15	20.8	80.0	8.24	1.32
99.0	4.88	25.4	80.0	4.12	2.36
99.0	4.12	32.1	80.0	2.77	3.47
90.0	1000	0.346	80.0	2.06	4.92
90.0	100	0.740	80.0	1.54	6.76
90.0	14.5	3.08	80.0	1.28	7.86
90.0	8.24	5.02	80.0	1.03	9.96
90.0	6.15	6.88	80.0	0.824	12.0
90.0	4.12	10.3	75.0	25.0	0.229
90.0	2.79	13.7	75.0	10.0	0.511
90.0	2.06	19.3	75.0	5.00	0.970
90.0	1.64	24.6	75.0	3.57	1.29
90.0	1.38	28.5	75.0	2.33	2.10
90.0	1.18	33.0	75.0	1.56	2.93
90.0	1.03	38.5	75.0	1.17	3.89

^{a} Concentration of $Cr(H_2O)_5(3\text{-pic})^{3+}$ varied in the range 1.6×10^{-5} to $1.9 \times 10^{-4}\,M$.
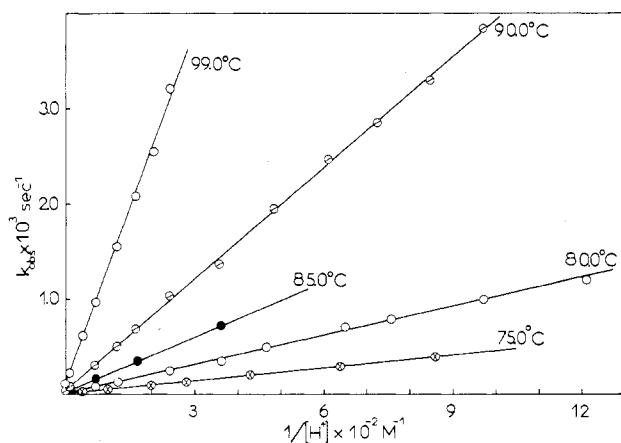
Figure 2. Plot of k_{obsd} *vs.* $1/(H^+)$ for the aquation of $Cr(H_2O)_5(3\text{-pic})^{3+}$ in $1.0\,M$ ionic strength $(NaClO_4)$ at different temperatures.

able in a simple preparative way. The ready formation of chromium(III) hydroxo- or oxo-bridged polynuclear complexes in weakly acidic and basic aqueous solutions makes the direct reaction between Cr^{3+} and ligand(s) very restrictive. The reaction of ferrous ion with base adducts of diperoxy-chromium(VI) species used in this work might prove useful as a method for preparation of monosubstituted chromium(III) complex ions with ligands having basic nitrogen or oxygen as the donor atom. Preliminary results show that the chromium(III) species with ligand being 3-chloropyridine, 3-cyano-pyridine, pyridine *N*-oxide, and 3-picoline *N*-oxide are formed in the respective reactions.[10]

The rate law of the same form as given by eq 3 has been found for the aquation of monosubstituted chromium(III) complex ions having an acidic ligand[11-15] as well as an amine ligand: ammine,[16] unidentate diethylenetriamine,[17]

unidentate tetraethylenepentamine,[18] and pyridine.[7] Analogous rate laws were also observed for the dissociation of the Cr-O bond in the Ru(II)-Cr(III) and Ru(III)-Cr(III) binuclear complexes bridged by substituted pyridines.[19] The failure to observe an inverse-acid term in the rate law for aquation of the complexes with unidentate ethylenediamine ligand[20] and with unidentate triethylenetetramine ligand[21] is most likely due to a narrow acidity range used.

The rate law is consistent with k_0 in eq 3 being the rate constant for the aquation of $Cr(H_2O)_5(3\text{-pic})^{3+}$ and $k'_{-1} = k_{-1}/K_h$ the rate constant for the aquation of the conjugate base $Cr(H_2O)_4(OH)(3\text{-pic})^{2+}$, where K_h is the equilibrium constant for the acid dissociation reaction

$$Cr(H_2O)_5(3\text{-pic})^{3+} \rightarrow Cr(H_2O)_4(OH)(3\text{-pic})^{2+} + H^+$$
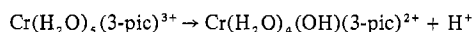
The interpretation assumes that $K_h/(H^+) \ll 1$ at the experimental conditions employed. This would not be true, however, if K_h and the corresponding ΔH had values similar or higher than those of hexaaquochromium(III) ion.[22] Unfortunately, a reliable K_h value for the complex ion studied is not available.

The pK_a's for the protonated forms of 3-picoline, pyridine, and 4-amidopyridine at 25° are 5.67, 5.21, and 3.61, respectively.[23,24] The specific rates for aquation of the corresponding monosubstituted chromium(III) complexes *via* the acid-independent path at 70° follow the same sequence ($k_0 \times 10^6$ in sec^{-1}: 2.5, 5.5, and 43, respectively[25]). Qualitatively, the reactivity parallels the basicity of the ligands.

Registry No. $(H_2O)_5Cr(3\text{-pic})^{3+}$, 36994-85-1.

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Exchange of Acetonitrile on Complexes of Nickel(II) and Cobalt(II) Formed with 2,2′,2″-Triaminotriethylamine and 2,2′,2″-Tri(*N,N*-dimethylamino)triethylamine

R. J. West and S. F. Lincoln*

Nickel(II) and cobalt(II) are six- and five-coordinated, respectively, in complexes formed with the tetradentate ligand 2,2′,2″-triaminotriethylamine (tren)[1,2] but are both

five-coordinated in complexes formed with 2,2',2''-tri(N,N-dimethylamino)triethylamine (Me$_6$tren).[3] This presents an opportunity to examine the effect of variation of metal ion coordination number, complex geometry, and ligand N-methylation on the rates of solvent-exchange processes and to gain mechanistic insight into such processes. A ^{14}N magnetic resonance and spectrophotometric study of the above systems in acetonitrile is reported here.

Visible Spectra

Spectra C and D in Figure 1 are those of solutions of [M(CH$_3$CN)$_6$](ClO$_4$)$_2$, where M = Co and Ni, respectively, in acetonitrile, containing equimolar amounts of tren. Spectrum C (ν_{max}, cm^{-1} (ϵ): 6200 (21.3), 14,900–15,400 (sh), 18,200 (101.7), 20,800 (53.0)) is similar to those of five-coordinated[3,4] [Co(tren)(NCS)]$^+$ and [Co(Me$_6$tren)X]$^+$, but is distinctly different from the spectra of [Co(CH$_3$CN)$_6$]$^{2+}$ and other six-coordinated cobalt(II) species[5] both in band absorption maxima (ν_{max}) and in molar absorbance (ϵ) values. This is consistent with [Co(tren)(CH$_3$CN)]$^{2+}$ being the predominant species in solution. Spectrum D (11,600 (17.5), 18,700 (13.1), 28,800 cm^{-1} (16.4)) is typical of six-coordinated nickel(II)[6] and the species in solution is formulated as [Ni(tren)(CH$_3$CN)$_2$]$^{2+}$. The Co(II)- and Ni(II)-tren complexes are also five- and six-coordinated, respectively, in water.[1] Spectra B (~5900 (~25), 15,200 (32.4), 17,600 (73.8), 20,800 cm^{-1} (63.6)) and A (8500 (22.6), 16,400 (64.8), 25,200 cm^{-1} (177.0)) are those of [M(Me$_6$-tren)(ClO$_4$)]ClO$_4$ where M = Co and Ni, respectively, in acetonitrile. In both cases the spectra are as expected for high-spin five-coordinated species and are characterized by different ν_{max} and greater ϵ values than those observed[3] for [M(Me$_6$tren)(ClO$_4$)]$^+$ in nitroethane (where perchlorate evidently remains in the fifth site in the first coordination sphere) which indicates displacement of perchlorate from the first coordination sphere to give [M(Me$_6$tren)(CH$_3$CN)]$^{2+}$.

The magnetic moments, μ_{eff}, for these species in acetonitrile solution, determined by the method of Evans[7] using toluene as the inert reference, are given in Table I.

[14]N Magnetic Resonance Data

The treatment of Swift and Connick[8] is used in the analysis of the ^{14}N line broadening and shift data for bulk acetonitrile solvent. Line broadening and shift data are expressed as in eq 1 and 2, respectively, where γ is the ^{14}N magnetogy-

$$T_{2p} = 2\gamma^{-1}(W_{obsd} - W_0)^{-1} \text{ (sec}^{-1}) \qquad (1)$$

$$S = [(\omega_{obsd} - \omega_0)/\omega_0] \times 10^6 \text{ (ppm)} \qquad (2)$$

ric ratio (1934 G^{-1} sec^{-1}), W_{obsd} is the full line width for the paramagnetic solution in gauss measured at half-maximum amplitude of the absorption signal, W_0 is the same quantity for the acetonitrile reference solution, ω_{obsd} is the ^{14}N frequency of bulk acetonitrile in the paramagnetic solution, and ω_0 is the same quantity in the reference solution.

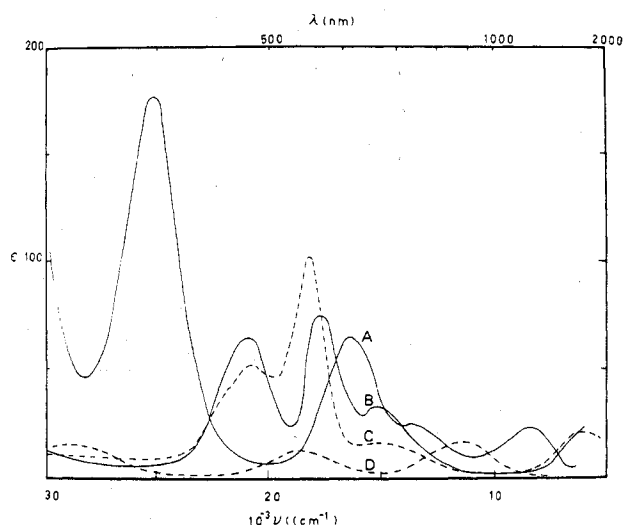The relaxation data for the [Ni(tren)(CH$_3$CN)$_2$]$^{2+}$ system

(1) P. Paoletti, M. Ciampolini, and L. Sacconi, *J. Chem. Soc.*, 3589 (1963).
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(7) D. F. Evans, *J. Chem. Soc.*, 2003 (1959).
(8) T. J. Swift and R. E. Connick, *J. Chem. Phys.*, 37, 307 (1962). We are indebted to a reviewer for a valuable comment on data-fitting procedures.

Figure 1. Absorption spectra in acetonitrile solution: A, [Ni(Me$_6$-tren)(CH$_3$CN)]$^{2+}$; B, [Co(Me$_6$tren)(CH$_3$CN)]$^{2+}$; C, [Co(tren)(CH$_3$-CN)]$^{2+}$; D, [Ni(tren)(CH$_3$CN)$_2$]$^{2+}$.

are consistent with acetonitrile exchanging on a site a at a rate several orders of magnitude less than on a second site b. The line broadening and shift data were accordingly fitted to eq 3 and 4, respectively, where $P_M = P_M'$ and is the mole

$$T_{2p} = \frac{\tau_M}{P_M}\left[\frac{(T_{2M}^{-1} + \tau_M^{-1})^2 + \Delta\omega_M^2}{T_{2M}^{-2} + (T_{2M}\tau_M)^{-1} + \Delta\omega_M^2}\right] + \frac{T_{2M}'}{P_M'} \qquad (3)$$

$$S = P_M\Delta\omega_M[(1 + \tau_M T_{2M}^{-1})^2 + \tau_M^2\Delta\omega_M^2]^{-1} + P_M'\Delta\omega_M' \qquad (4)$$

fraction of acetonitrile coordinated at sites a and b, respectively, in [Ni(tren)(CH$_3$CN)$_2$]$^{2+}$, $\Delta\omega_M$ and $\Delta\omega_M'$ are the differences between the resonant frequencies of ^{14}N in acetonitrile at sites a and b and bulk acetonitrile, $T_{2M} = T_{2M}'$ and is the acetonitrile ^{14}N transverse relaxation time at sites a and b, respectively (the equality $T_{2M} = T_{2M}'$ assumes identical Ni–N bond distances at sites a and b whereas they may differ by ~0.1 Å as discussed below), and τ_M is the mean residence time of acetonitrile at site a.

In fitting the T_{2p} data to eq 3 the A/h value from the shift data was used and the "activation energies" E_M for T_{2M} and T_{2M}' were constrained to be equal. The best fit of the T_{2p} data to eq 3 is shown in Figure 2. The shift data were fitted to eq 4 by substituting the best fit τ_M values from the T_{2p} data into eq 4. The best fit of the shift data is shown in Figure 2.

The temperature dependences of τ_M, T_{2M}, and T_{2M}', are given by eq 5 and 6, respectively. The derived parameters

$$\tau_M^{-1} = k_1 = \frac{kT}{h}\exp((-\Delta H^{\ddagger} + T\Delta S^{\ddagger})/RT) \qquad (5)$$

$$T_{2M}^{-1} = C_M\exp(E_M/RT) \qquad (6)$$

are given in Table I.

The line broadening and shift data for the [Co(tren)(CH$_3$-CN)]$^{2+}$ system (Figure 2) are consistent with rapid exchange of acetonitrile such that chemical-exchange processes do not modulate the ^{14}N relaxation rates and conform to the expressions $T_{2p} = T_{2M}P_M^{-1}$ and $S = P_M\Delta\omega_M$, respectively. As a consequence of this only a lower limit may be set for k_1 at 25°.

Equation 7[9] was used to calculate A/h values; S_e is the

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Table I. Solvent-Exchange and Magnetic Parameters in Acetonitrile Solution[e]

Complex	$10^{-3}k_1$, sec^{-1}	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, cal mol^{-1} deg^{-1}	E_M, kcal mol^{-1}	$10^{-6}A/h$, Hz	μ_{eff}, BM
[Ni(CH$_3$CN)$_6$]$^{2+}$ [c]	2.0 ± 0.3[j]	16.4 ± 0.5	12.0 ± 2.0			3.15[f]
[Ni(tren)(CH$_3$CN)$_2$]$^{2+}$ [a]	165 ± 35[j]	10.8 ± 1.5	1.4 ± 5.0	1.8	15.1	
				1.8	15.1	3.0
[Ni(tren)(CH$_3$CN)$_2$]$^{2+}$ [b]	≥2000[i]			1.8	15.1	
[Ni(Me$_6$tren)(CH$_3$CN)]$^{2+}$	≤0.1[h]					3.1
[Co(CH$_3$CN)$_6$]$^{2+}$ [d]	320 ± 30[j]	11.4 ± 0.5	5.2 ± 2.0		8.56	5.2[g]
[Co(tren)(CH$_3$CN)]$^{2+}$	≥2000[i]			3.3	7.03	4.7
[Co(Me$_6$tren)(CH$_3$CN)]$^{2+}$	~≤0.1[h]					4.0

[a] Site a. [b] Site b. [c] R. J. West and S. F. Lincoln, *Aust. J. Chem.*, **24**, 1169 (1971). [d] R. J. West and S. F. Lincoln, *Inorg. Chem.*, **11**, 1688 (1972). [e] [14]N data only. The errors quoted for the kinetic parameters are calculated directly from the mean of the residuals of the data fit. [f] A. E. Wickenden and R. A. Krause, *Inorg. Chem.*, **4**, 404 (1965). [g] B. J. Hathaway, D. G. Holah, and E. A. Underhill, *J. Chem. Soc.*, 2444 (1962). [h] At 80°. [i] At −40°. [j] At 25°.
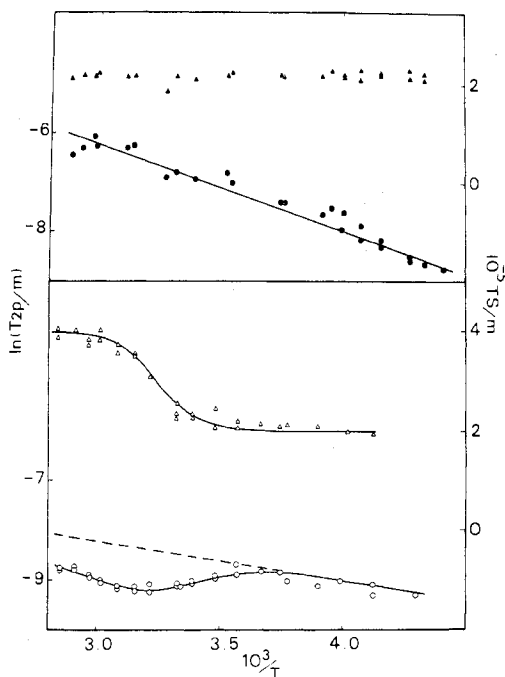

Figure 2. Nitrogen-14 relaxation and shift data. Nickel(II) relaxation data (open circles) and shift data (open triangles) fits are indicated by solid curves. The broken line is the T_{2M}' component of the data fit. The cobalt(II) relaxation and shift data are shown as closed circles and closed triangles, respectively.

$$\frac{\Delta\omega_M}{\omega_0} = \frac{-A[S_e(S_e + 1)]^{1/2}\mu_{eff}}{h(3kT)} \qquad (7)$$

electron spin of the paramagnetic species.

No ^{14}N broadening or shift was observed for bulk acetonitrile in the [M(Me$_6$tren)(CH$_3$CN)]$^{2+}$ solutions up to 0.4 m concentration of the complexes from 77 to −22° and it appears that k_1 at −22° must be <100 sec^{-1}.

Experimental Section

2,2′,2″-Triaminotriethylamine hydrochloride was obtained from Strem Chemicals Inc. and converted to the amine by standard procedures. Redistilled acetonitrile and tren were dried and stored over Linde 4A molecular sieves. The complexes M(CH$_3$CN)$_6$(ClO$_4$)$_2$ and [M(Me$_6$tren)ClO$_4$]ClO$_4$ where M is Ni and Co were prepared as reported.[3,10] Infrared spectra of concentrated Nujol mulls of the complexes exhibited no water peak in the 3500-cm^{-1} region.

In the presence of oxygen, Co(II)-tren solutions in acetonitrile undergo rapid oxidation, and consequently all solutions were prepared by mixing rigorously degassed solutions of [Co(CH$_3$CN)$_6$]$^{2+}$ in acetonitrile and solutions of tren in acetonitrile under vacuum. The other systems are not oxygen sensitive. All samples for ^{14}N nmr and the

Co(II)-tren samples for spectrophotometric determinations were sealed under vacuum. Other spectrophotometric solutions were contained in tightly stoppered cells.

[14]N nmr measurements were made on solutions in the range 0.3038–0.4699 m as described in the literature.[11] Spectrophotometric determinations were made on solutions in the range 0.00784–0.03595 M with a Unicam SP700 spectrophotometer.

Discussion

The two acetonitrile exchange rates observed for the nonequivalent sites on [Ni(tren)(CH$_3$CN)$_2$]$^{2+}$ are best considered in conjunction with X-ray structural data reported[2] for [Ni(tren)(NCS)$_2$], which is expected to exhibit similar geometry. Rasmussen reported Ni–N distances of 2.104 and 2.020 (±0.04) Å for NCS cis and trans to the tren tertiary nitrogen, respectively. Qualitative extension of this data to the acetonitrile system suggests that the cis CH$_3$CN ligand (b) may have the longer Ni–N bond length and hence be more labile than trans CH$_3$CN (a). The kinetic parameters for site a indicate considerable labilization of coordinated acetonitrile at 25°, by comparison to the data for [Ni(CH$_3$CN)$_6$]$^{2+}$—a similar trend is observed for the cobalt(II)-acetonitrile systems (Table I) and also in the analogous aquo systems.[12,13] Labilization of coordinated solvent by polydentate amine ligands may be rationalized by a model in which electron donation from the amine nitrogen atoms lessens the effective charge of the central metal ion thereby reducing $\Delta H^{\ddagger}$ and labilizing the solvent.[14] The apparent reduction of lability of Me$_6$tren indicates that an additional factor must be considered. Six- and five-coordination of nickel(II) and cobalt(II) in the tren complexes suggests sufficient flexibility for these species to be five- and six-coordinated, respectively, in the transition states of the extreme dissociative and associative acetonitrile exchange mechanisms. Exclusive five-coordination of [M(Me$_6$tren)Br]$^+$ (M = Mn, Fe, Co, Ni, Cu, Zn) suggests reduced flexibility and probable preclusion of significant expansion or geometric rearrangement in the transition state for cobalt(II) and nickel(II). In [Ni(tren)(CH$_3$-CN)$_2$]$^{2+}$ commensurate lengthening and shortening of Ni–N bonds at sites a and b are envisaged as being the gross characteristics of a largely dissociative transition state, while with [Co(tren)(CH$_3$CN)]$^{2+}$ solvent assistance in a dissociative interchange mechanism might well lead to a transition state geometrically similar to that for the nickel(II) system. On this basis it appears that the relatively inflexible Me$_6$tren ligand prevents close approach of solvent to the metal atom

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and the consequent reduction in solvent assistance drastically reduces lability.

Registry No. $[Ni(CH_3CN)_6]^{2+}$, 15554-59-3;] Ni(tren)-$(CH_3CN)_2]^{2+}$, 36805-39-7; $[Ni(Me_6tren)(CH_3CN)]^{2+}$, 36870-56-1; $[Co(CH_3CN)_6]^{2+}$, 16633-96-8; $[Co(tren)(CH_3CN)]^{2+}$, 36900-96-6; $[Co(Me_6tren)(CH_3CN)]^{2+}$, 36870-57-2; CH_3CN, 75-05-8.

Acknowledgments. We thank the Australian Research Grants Committee for supporting this study.

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Magnesium and Guanidinium Salts of a Silicon–Catechol Coordination Complex

D. W. Barnum,* J. M. Kelley, and B. Poocharoen

In a previous publication data on the preparation, composition, and structure of some ammonium salts of a silicon-catechol coordination complex were reported.[1] Here, we wish to report a new magnesium salt and additional information about the guanidinium salt.

Experimental Section

X-Ray powder diffraction patterns were measured with a General Electric XRD-5 spectrogoniometer using copper Kα radiation, a nickel filter, and a proportional counter for detection. Infrared frequencies were measured with a Beckman IR-12.

Magnesium trisilicate pentahydrate was purchased from Alfa Inorganics. Its X-ray powder diffraction pattern shows it to be amorphous. *Anal.* Calcd for $Mg_2Si_3O_8 \cdot 5H_2O$: Mg, 13.86; Si, 24.01. Found: Mg, 12.38, 12.47; Si, 23.31, 23.25. Resublimed catechol was purchased from Matheson Coleman and Bell and used without further purification.

Because basic catechol solutions are readily oxidized by atmospheric oxygen, all reactions were carried out under nitrogen using standard techniques that have been reviewed by Herzog, *et al.*[2]

Carbon, hydrogen, and nitrogen analyses were done by Huffman Laboratories, Wheatridge, Colo. Silicon was determined by decomposing and dehydrating with concentrated hydrochloric acid, filtering off the insoluble dehydrated silica, and igniting to SiO_2. Magnesium, when present, was determined in the filtrate by extracting the catechol into diethyl ether and titrating with EDTA using Eriochrome Black T indicator.

Magnesium Tris(catecholato)siliconate Nonahydrate. A 2.11-g portion of $Mg_2Si_3O_8 \cdot 5H_2O$ and 6.61 g of catechol (mole ratio $Si:H_2cat = 3:10$) were placed in a 250-ml flask. The flask was evacuated, filled with nitrogen, and 40 ml of solvent was added. Solvents used were 0.05 F acetic acid, 0.05 F potassium biphthalate, 1.0 F ammonium chloride, 0.05 F ammonia, and water. The contents of the flask were swirled until all of the catechol dissolved and then the mixture was set aside at room temperature. After about 1 month tabular brownish crystals of $Mg[Si(cat)_3] \cdot 9H_2O$ were formed that were several millimeters in diameter and were separated from unreacted magnesium trisilicate by picking them out with tweezers. The crystals were washed with water and blotted dry. The yield was 30–50%. Once the crystals are dry, they are stable for several weeks, or even months, in the open atmosphere without noticeable decomposition. However, if ground to a fine powder, the compound spontaneously loses lattice water and decomposes to a yellowish green grayish product in about 2 weeks.

The nonahydrate is best identified by its powder diffraction pattern which has strongest lines[3] at $d = 11.2$ (90), 8.5 (65), 8.1

(80), 5.52 (36), 5.06 (30), 4.83 (100), 4.66 (48), 4.53 (60), and 3.424 (37) A. *Anal.* Calcd for $Mg[Si(C_6H_4O_2)_3] \cdot 9H_2O$: C, 40.12; H, 5.47. Found: C, 39.74; H, 5.61. Weight loss for conversion to $Mg[Si(C_6H_4O_2)_3] \cdot 3H_2O$: calcd, 20.1%; found, 20.1, 20.4, 20.6%.

Magnesium Tris(catecholato)siliconate Trihydrate. Crystals of the nonahydrate dried to constant weight under vacuum at room temperature lose water of crystallization and crumble to a fine light brown powder of the trihydrate. About 40 hr is required to reach constant weight. *Anal.* Calcd for $Mg[Si(C_6H_4O_2)_3] \cdot 3H_2O$: C, 50.19; H, 4.21; Si, 6.52; Mg, 5.64. Found: C, 49.15; H, 4.27; Si, 5.96, 6.48, 6.29, 6.36; Mg, 5.68, 5.64, 5.59, 5.54. (Repeated values are analyses on different preparations.) The nmr is also in agreement with three waters. Four different preparations gave ratios of twelve phenyl protons to six OH protons.

The powder diffraction pattern of the trihydrate has principal lines at $d = 11.1$ (100), 10.3 (46), 6.41 (57), 6.23 (43), 5.93 (37), 5.55 (43), and 5.41 (30) A. The compound is hygroscopic, and as it picks up water, the line at 11.1 A is replaced by one at 11.4 A, the line at 7.46 A disappears, and the intensity of the 10.3-A line increases.

Magnesium Tris(catecholato)siliconate. The anhydrous salt was obtained by drying either the nonahydrate or the trihydrate for 160–220 hr under vacuum at 100°. The powder diffraction pattern has most intense lines at $d = 9.3$ (100), 8.3 (100), and 5.1 (90) A. All lines are broad, indicating poor crystallinity. Weight loss on drying the nonahydrate: calcd, 30.1%; found, 30.2, 30.9%.

Diguanidinium Tris(catecholato)siliconate Monohydrate. Two methods of preparation were used. In the first method 13.2 g of catechol, 4.2 g of magnesium trisilicate, $Mg_2Si_3O_8 \cdot 5H_2O$, and 80 ml of water were stirred together overnight. The undissolved magnesium trisilicate was then filtered off and 40 ml of 1.0 F guanidinium chloride was added to the filtrate. A pale yellow precipitate began to form within a few minutes. After at least 3 hr the precipitate was filtered off, washed with water, and dried under vacuum at room temperature to constant weight. The yield was about 2.5 g.

In the second method of preparation, 200 ml of concentrated (15 F) ammonia was stirred overnight with 3.0 g of powdered silicic acid. The undissolved silicic acid was filtered off and 15.0 g of catechol was added to the filtrate. After all of the catechol dissolved 35 ml of 4.0 F guanidinium chloride was added. The precipitate was filtered, washed, and dried as described above. The yield was about 1.5 g.

Anal. Calcd for $(CN_3H_6)_2[Si(C_6H_4O_2)_3] \cdot H_2O$: Si, 5.73; C, 48.97; H, 5.34; N, 17.13. Found for four different preparations: Si, 5.81, 5.96, 6.25, 5.80; C, 50.39, 48.53, 49.69, 49.04; H, 5.24, 5.01, 5.27, 5.27; N, 17.18, 16.71, 16.56, 17.21.

The ratio of phenyl protons to OH and NH protons is 12:14 for a monohydrated guanidinium salt. Observed values were 12:14.0, 12:14.4, and 12:14.0 in dimethyl sulfoxide and 12:13.0, 12:13.6, and 12:13.8 in dimethylformamide.

The X-ray powder diffraction pattern shows strongest lines (with relative intensities ≥30) at $d = 10.0$ (100), 8.9 (45), 8.0 (84), 7.52 (36), 6.25 (36), 5.32 (30), 5.17 (54), 5.01 (60), 4.10 (100), 4.04 (97), 3.477 (64), 3.373 (30), 3.312 (30) A.

The dry compound is slightly hygroscopic and begins to discolor after about 1 month in air. The solubility is 0.5 g/100 ml in water, at least 12 g/100 ml in dimethyl sulfoxide, and at least 32 g/100 ml in dimethylformamide. In other common organic solvents it is insoluble.

Results and Discussion

Nearly neutral aqueous solutions of catechol react at room temperature with amorphous magnesium trisilicate to form crystals of $Mg[Si(cat)_3] \cdot 9H_2O$

$$Mg_2Si_3O_8 \cdot 5H_2O + 9H_2cat + 5H_2O = 2H^+ + 2Mg[Si(cat)_3] \cdot 9H_2O + Si(cat)_3{}^{2-} \qquad (1)$$
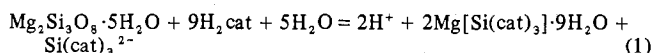
Under the conditions used (*i.e.*, $[H_2cat] \approx 1.0 M$ and pH ~ 6.4), one can calculate from the formation constant[4,5] that any silicon in solution will be present as $Si(cat)_3{}^{2-}$ rather than $Si(OH)_4$. Thus, in eq 1 the unprecipitated silicon appears on the right-hand side as $Si(cat)_3{}^{2-}$.

(1) D. W. Barnum, *Inorg. Chem.*, 11, 1424 (1972).

(2) S. Herzog, J. Dehnert, and K. Luhder, "Technique of Inorganic Chemistry," Vol. VII, H. B. Jonassen and A. Weissberger, Ed., Interscience, 1968, pp 119–149.

(3) Relative intensities are given in parentheses. Only lines with intensities ≥30 are tabulated.

(4) H. Bartels, *Helv. Chim. Acta*, 47, 1605 (1964).

(5) H. Baumann, *Beitr. Silikose-Forsch., Sonderbd.*, 4, 43 (1960).