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.

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Magnesium and Guanidinium Salts of a Silicon-Catechol Coordination Complex

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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) Å. *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) Å. The compound is hygroscopic, and as it picks up water, the line at 11.1 Å is replaced by one at 11.4 Å, the line at 7.46 Å disappears, and the intensity of the 10.3-Å 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) Å. 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) Å.

The dry compound is slightly hydroscopic 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 $Mg[Si(cat)_3] \cdot 9H_2O$

$$Mg_2Si_3O_8 \cdot 5H_2O + 9H_2cat + 5H_2O = 2H^+ + 2Mg[Si(cat)_3] \cdot 9H_2O + Si(cat)_3{}^{2-} \quad (1)$$

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 $Si(cat)_3{}^{2-}$.

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(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.

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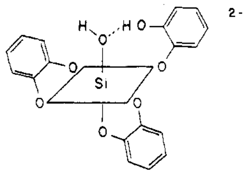
If the nonahydrate is taken to constant weight by drying under vacuum at room temperature, the crystals crumble to a fine light brown powder of Mg[Si(cat)$_3$]·3H$_2$O. Under severe drying conditions, *i.e.*, more than 160 hr at 100° under vacuum, anhydrous Mg[Si(cat)$_3$] is obtained.

The analytical data and integrated nmr intensities obtained on the guanidinium salt are in good agreement with a complex containing one molecule of "water of crystallization." Rosenheim, *et al.*,[6] reported the same salt with seven waters of crystallization and Weiss, *et al.*,[7] found two waters. However, neither of these groups dried their product to constant weight. Apparently their products were dried in air but it was found in this work that the "monohydrate" is slightly hygroscopic.

The structure of silicon-catechol complexes containing "water of crystallization" is still in question. Flynn and Boer[8] have determined the structure of the anhydrous dipyridinium salt, (pyH)$_2$[Si(cat)$_3$], by X-ray diffraction. The silicon is octahedrally coordinated and each catechol is a bidentate ligand as one would expect. However, for those complexes containing strongly held water there is evidence for structure I which was discussed earlier in connection with the ammonium salts.[1] One of the pieces of evidence was the tendency of catechol complexes with silicon, titanium, germanium, and iron(III) to hold strongly one molecule of water. The guanidinium salt described here also fits this pattern. Thus, heating (CN$_3$H$_6$)$_2$[Si(cat)$_3$]·H$_2$O at 80° under vacuum for 200 hr resulted in a weight loss greater than expected for the loss of one water but the ir spectrum still showed an O-H stretching band and the X-ray diffraction pattern was still mainly that of the "monohydrate." The magnesium salt, however, holds three waters tightly. A possible structure is [Mg(OH$_2$)$_2$][Si(OH)(Hcat)(cat)$_2$].



I, Si(OH)(Hcat)(cat)$_2$-

Those compounds containing "water of crystallization" show a sharp infrared absorption band in the region of free or weakly associated OH groups that may be due to the SiOH group in structure I. This band occurs in (NH$_4$)$_2$[Si(cat)$_3$]·H$_2$O, at 3545 cm^{-1}, in (CN$_3$H$_6$)$_2$[Si(cat)$_3$]·H$_2$O at 3570 cm^{-1}, in Mg[Si(cat)$_3$]·3H$_2$O at 3551 cm^{-1}, and in Mg[Si(cat)$_3$]·9H$_2$O at 3555 cm^{-1} (or perhaps 3531 cm^{-1}). None of these frequencies corresponds to an overtone or combination band and such a band is absent in the anhydrous pyridinium and magnesium salts. However, the anhydrous pyridinium salt, (C$_5$H$_6$N)$_2$[Si(cat)$_3$], which is hygroscopic, develops a sharp band at 3496 cm^{-1} when exposed to moist air.

Another feature of interest in the infrared spectra is a pair of bands located at about 1100 and 1020 cm^{-1} that are probably C-H in-plane bending. In free catechol they are found at 1104 and 1049 cm^{-1}, a separation of 55 cm^{-1}. Upon complexing with silicon, however, the 1049-cm^{-1} band shifts about 25 cm^{-1} to lower frequency and the separation between the two bands increases to approximately 80 cm^{-1}.

Registry No. Mg[Si(cat)$_3$]·9H$_2$O, 37474-58-1; Mg[Si(C$_6$H$_4$O$_2$)$_3$]·3H$_2$O, 37474-59-2; (CN$_3$H$_6$)$_2$[Si(C$_6$H$_4$O$_2$)$_3$]·H$_2$O, 37474-60-5; magnesium tris(catecholato)siliconate, 37498-56-9.

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