the spectral observations. The substantial changes from the solid-state spectra which occur on dissolution of $Co[OC(NH_2)_2]_6(ClO_4)_3$ in urea-saturated water indicate that the cationic complex does not survive intact for any appreciable time in this medium. The observed spectral shifts suggest that the initial product is a substantially hydrolyzed (and perhaps dimerized) cobalt(III) complex. The cobalt is ultimately reduced to cobalt(II) *via* a urea-inhibited path(s).[9]

The most potentially important aspect of this work is the contribution of two new members to a class of compounds which deserve serious consideration as synthetic intermediates, especially in water-sensitive, nonaqueous applications. (Dry acetonitrile is the most useful solvent thus far employed.) Three advantages seem obvious. They can be easily prepared as stable, anhydrous salts. As perchlorate salts they contain a poorly coordinating anion. (Caution should be excercised with potentially explosive perchlorates.) Urea, being weakly bound, can be readily substituted and seems to offer similar advantages to those of trialkyl phosphate ligands.[10] Such application is exemplified by the work of Summers and Stoufer[4] and by our related observations[11] that the dimeric, red vanadium(III)–2,2′-bipyridine species obtained in aqueous media[12] can be avoided by using $V[OC(NH_2)_2]_6(ClO_4)_3$ with bipyridine in dry acetonitrile.

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[9] M. Anbar and I. Pecht, *J. Amer. Chem. Soc.*, **89**, 2553 (1967), reported studies of $Co(H_2O)_6^{3+}$ reduction.

[10] (a) R. B. Jordon, A. M. Sargeson, and H. Taube, *Inorg. Chem.*, **5**, 1091 (1966); (b) D. A. Buckingham, L. G. Marzilli, and A. M. Sargeson, *J. Amer. Chem. Soc.*, **89**, 2772 (1967).

[11] P. Eisenhardt and L. E. Bennett, unpublished work.

[12] L. E. Bennett and H. Taube, *Inorg. Chem.*, **7**, 254 (1968).

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Catechol Complexes with Silicon

BY DENNIS W. BARNUM

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In the course of an investigation of water-stable silicon complexes it was found that much of the information in the literature about silicon complexes with catechol is either incorrect or must be modified.

Rosenheim, Raibman, and Schendel[1] reported the preparation of $(NH_4)_2[Si(C_6H_4O_2)_3]\cdot 9H_2O$ by treating freshly precipitated silica gel with catechol in hot ammonium hydroxide solution. Weiss, Reiff, and Weiss[2] used a similar procedure but claimed that the product is dimeric $(NH_4)_4[Si_2(C_6H_4O_2)_6]\cdot 9H_2O$. Despite all efforts in the present work to repeat the procedure of Weiss, *et al.*, exactly (even using colloidal silica from the same commercial source) neither the composition reported by Weiss, *et al.*, nor by Rosenheim, *et al.*, resulted. Instead clear colorless crystals that contain ammonia of crystallization were obtained. They have the general composition $(NH_4)_2[Si(C_6H_4O_2)_3]\cdot xH_2O\cdot yNH_3$, where $x = 1$ or 2 and $y = 2$–4. Exact values of x and y have not been determined because the crystals begin to effloresce ammonia as soon as they are removed from the mother liquor. Furthermore, the amount of ammonia appears to depend on its concentration in the solution from which the crystals formed. As the crystals lose ammonia they crumble to a fine white powder.

The analytical data presented by Weiss, *et al.*, and by Rosenheim, *et al.*, rule out the possibility that they mistook ammonia of crystallization for water. Apparently, different products are obtained depending on the conditions of the precipitation, but these have not yet been discovered.

Ammonia of crystallization is evident from the fact that one can smell ammonia over the product even after it has been thoroughly washed free of the mother liquor and dried (although not dried to constant weight). Also, the product can be taken to constant weight in a slow stream of nitrogen and the ammonia measured by passing the nitrogen through 4% boric acid solution and then titrating the ammonia with standard hydrochloric acid. In another experiment, the initial product contained 11.0% N after washing with acetone and then ether and then drying for 2 hr in a stream of anhydrous ammonia. After 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 this work the crystals were taken to constant weight either by removing the ammonia of crystallization with a slow stream of nitrogen (which requires 5–7 days at room temperature) or by 1–4 hr under vacuum (<1 Torr) at room temperature. The use of elevated temperatures may cause discoloration. Also, some unreacted catechol is a common impurity and this was removed by leaching the dried product with diethyl ether. The *usual* product analyzes for a "monohydrate," *i.e.*, $(NH_4)_2[Si(C_6H_4O_2)_3]\cdot H_2O$. In the following analytical data repeated numbers represent different preparations. *Anal.* Calcd for $(NH_4)_2[Si(C_6H_4O_2)_3]\cdot H_2O$: Si, 6.91; C, 53.18; H, 5.46; N, 6.89. Found: Si, 6.81, 7.01, 6.93, 7.01, 6.98; C, 52.39, 53.04, 52.01, 52.95; H, 5.56, 5.49, 5.49, 5.32; N, 6.48, 6.58, 6.67, 6.15.

The "monohydrate" probably has structure I. Evidence for this structure is that the "water of hydration" *cannot* be removed by heating the complex for 2 weeks

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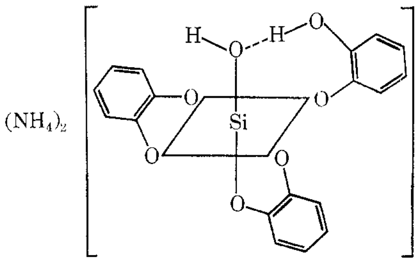
[1] A. Rosenheim, B. Raibman, and G. Schendel, *Z. Anorg. Allg. Chem.*, **196**, 160 (1931).

[2] A. Weiss, G. Reiff, and A. Weiss, *ibid.*, **311**, 151 (1961).



I

under vacuum (<1 Torr) at 60°. Discoloration occurs but X-ray powder diffraction shows that the material is still predominantly the "monohydrate." In the infrared absorption spectrum there is a sharp band at 3545 cm^{-1} which is characteristic of a free or weakly associated –OH group. Also, the nmr spectrum shows aromatic ring protons at τ 3.77 ppm, ammonium ion protons at τ 4.4–5.6 ppm depending on the concentration of the complex and the water content of the solvent, and *two* –OH protons at τ 3.30 and 3.46 ppm relative to TMS. Craddock and Jones[3] assigned this same structure to an arsenic(V) complex with catechol; $H[As(C_6H_4O_2)_3]\cdot H_2O$. Also, "chelation" by catechol through a hydrogen bond, as in structure I, has been established in a nickel(II)–catechol complex by X-ray diffraction.[4] The formula for this compound would be more correctly written as $(NH_4)_2[Si(OH)(C_6H_5O_2)(C_6H_4O_2)_2]$.

Weiss, Reiff, and Weiss[2] suggested a dimeric structure for the $Si(C_6H_4O_2)_3{}^{2-}$ anion. Conductivity studies are being made on the compounds prepared in this work. The one datum available so far (in dimethyl sulfoxide) indicates a monomeric structure for the $Si(OH)(C_6H_5O_2)(C_6H_4O_2)_2{}^{2-}$ ion.

Further evidence for structure I came from attempts to repeat the preparation of anhydrous $(NH_4)_2[Si(C_6H_4O_2)_3]$ from $SiCl_4$ as reported earlier by Rosenheim and Sorge.[5] The first attempts in this laboratory gave the "monohydrate." However, by rigorous exclusion of water a compound that analyzes correctly for $(NH_4)_2[Si(OC_2H_5)(C_6H_5O_2)(C_6H_4O_2)_2]$ was obtained. *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, 6.49; C, 54.23; H, 6.34; N, 6.42. The structure is probably similar to that shown above for the "monohydrate." That is, the Si–OH group is replaced by an $Si{-}OC_2H_5$ group and one of the three catechol molecules is attached to the $Si{-}OC_2H_5$ group by a hydrogen bond. Reexamination of the analytical data presented by Rosenheim and Sorge indicates that they had prepared the "monohydrate" rather than the anhydrous salt. *Anal.* Calcd for $(NH_4)_2[Si(OH)(C_6H_5O_2)(C_6H_4O_2)_2]$: Si, 6.91; $NH_4{}^+$, 8.88. Calcd for $(NH_4)_2[Si(C_6H_4O_2)_3]$: Si, 7.23; $NH_4{}^+$, 9.29. Found by Rosenheim and Sorge: Si, 7.04; $NH_4{}^+$, 8.88.

It was mentioned above that $(NH_4)_2[Si(OH)(C_6H_5O_2)(C_6H_4O_2)_2]$ is the *usual* product from the reaction of catechol with silicic acid or colloidal silica in ammonium hydroxide solution after taking the initial colorless crystals to constant weight. In some preparations the X-ray powder diffraction pattern of the product showed the presence of a substantial amount of an impurity even though the infrared absorption spectrum showed nothing amiss. Upon two occasions the product was nearly free of the "monohydrate." Analytical data suggest a compound containing 4 mol of catechol per mole of silicon, *i.e.*, $(NH_4)_2[Si(OH)(C_6H_5O_2)(C_6H_4O_2)_2]\cdot C_6H_6O_2$. *Anal.* Calcd for $(NH_4)_2[Si(OH)(C_6H_5O_2)(C_6H_4O_2)_2]\cdot C_6H_6O_2$: Si, 5.44; C, 55.80; H, 5.46; N, 5.42. Found: Si, 5.41, 5.49, 5.52; C, 55.47, 54.84; H, 5.76, 5.58, 5.47; N, 6.39, 5.73, 5.84. The preparation of this compound requires 6–9 mol of catechol per mole of silicon in the reaction medium but it has not yet been obtained completely free from the "monohydrate." It is characterized by a very intense reflection at $2\theta = 9.15°$ in the X-ray powder diffraction pattern whereas structure I is characterized by two strongest reflections at $2\theta = 7.8$ and 15.5°.

Weiss, Reiff, and Weiss[2] also reported a complex containing 7 mol of catechol and 2 mol of silicon, *i.e.*, $(NH_4)_4[Si_2(C_6H_4O_2)_7]$. They precipitated this compound from a solution in mixed water–ethanol solvent. Compounds were also obtained in this work from a water–ethanol solvent but their nmr spectrum shows one ethyl group per mole of silicon and the compound should be formulated as $(NH_4)_2[Si(OH)(C_6H_5O_2)(C_6H_4O_2)_2]\cdot C_2H_5OH$. *Anal.* Calcd for $(NH_4)_2[Si(OH)(C_6H_5O_2)(C_6H_4O_2)_2]\cdot C_2H_5OH$: Si, 5.54; C, 47.42; H, 6.76; N, 5.53. Found (this work): Si, 5.65, 5.77; C, 47.20; H, 6.59; N, 5.87. Found (Weiss, Reiff, and Weiss): Si, 5.67; C, 47.9; H, 6.61; N, 5.50.

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Electron Paramagnetic Resonance Investigations of Some Copper(II) Dialkyldithiophosphate Complexes

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Dithiophosphate compounds are important in the inhibition of hydrocarbon oxidation. To clarify the mechanism of their action the investigation of their structure is necessary. In the present paper the structure of the copper(II) dialkyldithiophosphate complexes is studied by means of their epr and electronic spectra.