nitrosyl group while the other three iron atoms bond only to two sulfur atoms, one iron atom, and two nitrosyl groups. This effectively leads to a lower s-electron density at the Fe_I nucleus than at the Fe_{II} nucleus or, in terms of Mössbauer parameters, a more positive isomer shift. Furthermore, the d-electron back-donation from electrons on the iron atoms into the nitrosyl π orbitals would, through shielding effects, cause a lowering of s-electron density at the iron nucleus. This back-bonding is stronger in the apical iron–nitrosyl bond as indicated by both the shorter Fe–N bond and the longer N–O bond on the apical iron nitrosyl contributing to the increased isomer shift. As is to be expected from the lower symmetry of the Fe_{II} atoms, their quadrupole splitting is larger.

Both the Mössbauer and infrared data support the X-ray crystallographic strcuture for the black Roussinate ion—two different iron atoms and the presence of terminal nitrosyl groups.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF FLORIDA, GAINESVILLE, FLORIDA 32601

Synthesis and Characterization of Urea Complexes of Cobalt(III)

BY LARRY E. BENNETT

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Hexaurea complexes of Ti(III),[1] V(III),[2] Cr(III),[3] Mn(III),[4] and Fe(III)[5] have attracted considerable spectroscopic attention. Further, the manganese complex has recently found an intriguing application as a synthetic intermediate in the nonaqueous preparation of previously unknown Mn(III) complexes containing six nitrogen donor atoms.[4] In this context we wish to report the synthesis and partial characterization of $Co[OC(NH_2)_2]_6(ClO_4)_3$, an easily handled, anhydrous, substitution-labile cobalt(III) source (desiccator life >18 months), which logically extends the Ti–Fe sequence. We also describe $(NH_3)_5Co[OC(NH_2)_2](ClO_4)_3$. These results provide compounds of potential utility as synthetic intermediates as well as further spectroscopic data on urea complexes.

Experimental Section

$Co[OC(NH_2)_2]_6(ClO_4)_3$.—Perchloric acid (70–72%) was saturated with urea (~10 ml of $HClO_4$ and ~13 g of urea), then with sodium perchlorate, and again with urea. $Co(ClO_4)_2 \cdot 6H_2O$ (6.3 g) dissolved in a minimum amount of 2 *M* $HClO_4$ (final volume ~11 ml) was electrolytically oxidized using a platinum cup, immersed in an ice bath, as both container and anode and a platinum wire as the cathode. The blue-purple solution (still containing some Co(II)) obtained after extended electrolysis was added dropwise, with stirring, to the urea–perchloric acid solution at 0°. During the Co(III) addition, additional urea and sodium perchlorate were added to maintain high concentrations. The resulting murky suspension was filtered, yielding a pinkish red filtrate and a bright green solid which was thoroughly washed with small portions of ice-cold absolute ethanol until no red color wss evident in the washings and then dried under vacuum. *Anal.* Calcd: C, 10.18; N, 23.75; H, 3.39; Co, 8.33. Found: C, 10.00; N, 23.37; H, 3.33; Co, 7.95 (by atomic absorption). Allowance for 1.2% occluded $NaClO_4$ (by atomic emission, courtesy of Mr. Ron Miller) brings these values to 10.1, 23.6, 3.37, and 8.05. After correction for nonmetal components, the "residual paramagnetism" of Co(III) is 36×10^{-5} cgsu (20°) leading to $\mu_{eff} = 0.95$ BM. Infrared absorption (excluding Nujol and perchlorate contributions) occurs at 3480 (s), 3360 (s), 3220 (sh), 1620 (s), 1527 (s), 1503 (s), 770 (w, sh), 756 (w, sh), 730 cm^{-1} (w). The compound dissolves in water with rapid loss of color and reduction to Co(II). In water saturated with urea, the low-energy visible absorption decays with $t_{1/2} \cong 50$ min (25°). Extrapolation to time of dissolution yielded λ (ϵ): 613 (30), 330 nm (340) (as poorly defined shoulder on high-energy absorption). In contrast, a Kel-F mull spectrum of the solid reveals a different absorption pattern [λ: 660, 470, ~350 nm (the last a poorly defined shoulder)].

$Co(NH_3)_5[OC(NH_2)_2](ClO_4)_3$.—$Co(NH_3)_5(H_2O)(ClO_4)_3$ (1 g) in 6 ml of urea-saturated water was stirred for 2.5 hr at 65° during which time the solution darkened considerably without appearing to change color. After storage at −10° for ~12 hr, 1 ml of 70% $HClO_4$ was added dropwise with stirring and the resulting small amount of solid was filtered off. Addition of *ca.* 20 ml of ethanol to the filtrate resulted, after 10 min of standing in an ice bath, in a precipitate which was filtered, washed with ethanol and ether, and vacuum dried to yield a pale red solid. *Anal.* Calcd: C, 2.39; H, 3.78; N, 19.53. Found: C, 2.59; H, 3.87; N, 19.55. The urea components of the infrared absorption are quite similar to those reported above for the hexaurea complex. Visible spectral data in water for this less labile complex yielded λ (ϵ): 503 (93), 345 nm (135) (a shoulder) (while generation of this complex seems assured by the described procedure, successful isolation seems dependent on poorly understood variables with acceptable product not being obtained on every attempt).

Discussion

Our infrared and magnetic measurements indicate for both cases that urea is coordinated through oxygen[3d] to an essentially diamagnetic Co(III) center. Spectral comparison with $Co(H_2O)_6^{3+}$ [λ(ϵ): 605 (36), 405 nm (45)[6]] and $Co(NH_3)_5H_2O^{3+}$ [λ(ϵ): 490 (47.0), 345 nm (44.1)[7]] suggests a lower spectrochemical position for urea relative to water on Co(III) in concert with the earlier studies.[1–5] The relatively high residual paramagnetism of Co(III) in the hexaurea compound[8] may be due to a closer approach to the spin state crossover point than for $Co(H_2O)_6^{3+}$,[8b] a veiw consistent with

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[1] (a) H. Hartmann, H. L. Schlafer, and K. H. Hansen, *Z. Anorg. Allg. Chem.*, **289**, 40 (1957); (b) R. Dingle, *J. Chem. Phys.*, **50**, 545 (1969).

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[3] (a) P. Pfeiffer, *Chem. Ber.*, **36**, 1927 (1903); (b) R. Dingle, *J. Chem. Phys.*, **50**, 1952 (1969); (c) C. E. Shaffer and C. K. Jørgensen, *J. Inorg. Nucl. Chem.*, **8**, 143 (1958); (d) R. B. Penland, S. Mizushima, C. Curran, and J. V. Quagliano, *J. Amer. Chem. Soc.*, **79**, 1575 (1957).

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[6] G. Hargreaves and L. H. Sutcliffe, *Trans. Faraday Soc.*, **51**, 786 (1955).

[7] A. Zwickel and H. Taube, *J. Amer. Chem. Soc.*, **83**, 793 (1961).

[8] (a) J. L. Kernahan and M. J. Sienko, *ibid.*, **77**, 1978 (1955); (b) H. L. Friedman, J. P. Hunt, R. A. Plane, and H. Taube, *ibid.*, **73**, 4028 (1951); suggested typical values for "low-spin" Co(III) of (5–20) $\times 10^{-5}$ cgsu.

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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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
PORTLAND STATE UNIVERSITY, PORTLAND, OREGON 97207

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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