constants *k* or H_2O exchange decrease with decreasing bond lengths. The same trend is observed for the corresponding activation enthalpies (Table V). This trend is analogous to that observed for the hydrolysis of organic ketals[42] and indicates that bond length is one of the rate-determining factors in a dissociation reaction.

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Registry No. $[Ni(tach)_2]^{2+}$, 31724-12-6; $[Ni(tach)(H_2O)_3](NO_3)_2$, 78654-70-3; $[Ni(tach)(H_2O)_3]^{2+}$, 25625-39-2; $[Ni(tach)(en)(H_2O)](ClO_4)_2$, 87655-59-2.

Supplementary Material Available: A description of crystal data, details of intensity measurements and of structure analysis, listings of atomic coordinates and vibrational parameters and selected bond lengths, bond angles, and torsion angles for $[Ni(tach)(H_2O)_3{}^{2+}](NO_3)_2$, a half normal probability plot comparing positional parameters determined in ref 11 and in this work, and a table of observed and calculated structure factors (18 pages). Ordering information is given on any current masthead page.

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Base-Catalyzed Hydration of Cobalt(III)-Coordinated Dimethylcyanamide and Linkage Isomerization of the Derived N-Bound Dimethylurea Complex

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The dimethylcyanamide complex ion $[(NH_3)_5CoNCN(CH_3)_2]^{3+}$ has been synthesized and the rate law for its base hydrolysis established: $-d[\text{complex}]/dt = k_{OH}[\text{complex}]$; $k_{OH} = 3.06 \pm 0.03$ M^{-1} s^{-1} (25 °C, $\mu = 1.0$ M (KCl)). The many-fold rate enhancement for the hydrolysis of the substituted nitrile on coordination to Co(III) is discussed in relation to data for other nitriles. The hydrolysis product, the deprotonated dimethylurea complex $[(NH_3)_5CoNHCON(CH_3)_2]^{2+}$, has been isolated. It is stable in basic solution but rapidly isomerizes to its O-bonded linkage isomer $[(NH_3)_5CoOC(NH_2)N(CH_3)_2]^{3+}$ in acid solution; only a little (~3%) competitive hydrolysis (to yield $[(NH_3)_5CoOH_2]^{3+}$ and $NH_2CON(CH_3)_2$) is observed. Kinetic data for the pH region 0–5 establish the rate law $-d[\text{complex}]/dt = k[H^+]/(K_a' + [H^+])$, where $k = (1.60 \pm 0.02) \times 10^{-2}$ s^{-1}, $pK_a' = 2.92 \pm 0.03$ ($\mu = 1.0$ M (KCl), 25 °C), $\Delta H^{\ddagger} = 80.9$ kJ/mol, and $\Delta S^{\ddagger} = -7.7$ J/(deg mol). The pK_a' value for the reactive entity in this urea-*N* to urea-*O* linkage isomerization reaction, the $[(NH_3)_5CoNH_2CON(CH_3)_2]^{3+}$ ion, agrees well with that determined independently, 2.89 ± 0.04. The site of protonation, at the bound N or exo-O atom, and the mechanism of the rearrangement process are discussed in relation to corresponding data for analogous amide and other systems. The oxygen-bonded dimethylurea complex hydrolyzes slowly to give the corresponding aqua or hydroxo product and free ligand. There is no detectable (<1%) hydrolysis of the ligand (C–N cleavage) to produce oxygen-bonded carbamate and free amine. The rate law $-d[\text{complex}]/dt = [k_x + k_{OH}K_w/([H^+] + K_a')][\text{complex}]$ is established; at 25 °C ($\mu = 1.0$ M ($NaClO_4$)), $k_s = 3.8 \times 10^{-5}$ s^{-1}, $k_{OH} = 10.3$ M^{-1} s^{-1}, and $pK_a' = 13.48$. The acid–base process corresponds to net deprotonation of the ligand in strong OH^- to give $[(NH_3)_5CoOC(NH)N(CH_3)_2]^{2+}$, and this ion is argued to be relatively unreactive. Comparisons are made with the previously studied urea-*O* and sulfamate-*O* systems. Proton and carbon-13 NMR data are presented that establish the ground-state structures of the dimethylurea-*O* and -*N* complexes and related derivatives. Restricted rotation about the $C\overset{\cdots}{-}N(CH_3)_2$ bond, induced by coordination to Co(III), is observed in the low-temperature ^1H NMR spectra of the oxygen-bonded and protonated-nitrogen-bonded dimethylurea complexes.

Introduction

In attempts to mimic aspects of the chemistry of the nickel metalloenzyme jack bean urease,[2,3] we are currently examining the H^+- and OH^--promoted reactions of a number of Co(III) and Rh(III) complexes of N- and O-coordinated ureas.[4] The enzyme is a very efficient catalyst of the hydrolysis of urea to produce ammonia and carbonic acid.[5] It contains 2 mol of Ni(II)/mol of active sites,[2,3] and at least one of these metal ions is involved in its mechanism of action.[6,7] An hypothesis for its detailed mechanism has recently been presented.[7] It involves nucleophilic attack by OH^-, coordinated to one Ni(II) ion, on urea which is coordinated to the other nickel ion through its carbonyl oxygen. In our previous examination of the base-catalyzed hydrolysis of the [(urea)pentaammine-cobalt(III)]$^{3+}$ ion, we found that O coordination of urea to cobalt(III) did not provide sufficient activation of the carbonyl group to enable the anticipated urea hydrolysis (to produce the $[(NH_3)_5CoO_2CNH_2]^{2+}$ ion) to compete with the facile base-catalyzed (S_N1CB) hydrolysis of the cobalt–oxygen bond.[4a] We sought to prepare the corresponding N-bonded urea complex to comment on the alternative possibility that urea might N coordinate with Ni(II) at the active site of urease

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and that this might be the reactive complex.

Reaction of urea with the $[(NH_3)_5CoOSO_2CF_3]^{2+}$ ion in sulfolane produces exclusively the O-bound linkage isomer,[8] and attempts to produce the $[(NH_3)_5CoNH_2CONH_2]^{3+}$ ion by various standard routes[9] have failed. For example, coordinated acetonitrile hydrates in a base-catalyzed reaction to produce the (deprotonated) acetamide complex,[10] and we sought to prepare N-bound urea by an analogous reaction of $[(NH_3)_5CoN{\equiv}C{-}NH_2]^{3+}$.[8] The unsubstituted cyanamide complex (orange) deprotonates under basic conditions ($pK_a' = 5.2$[11]) to produce the red carbodiimide complex $[(NH_3)_5CoN{=}C{=}NH]^{2+}$, which is resistant to nucleophilic attack by OH^-. However, in the dimethylcyanamide complex, $[(NH_3)_5CoN{\equiv}C{-}N(CH_3)_2]^{3+}$, deprotonation is blocked and this ion retains its orange color under mildly basic conditions. At higher pH it reacts rapidly and quantitatively with OH^- to produce the desired N-bound dimethylurea complex $[(NH_3)_5CoNHCON(CH_3)_2]^{2+}$ in its deprotonated form.

In this article, we present the kinetic details of this reaction and report upon the chemistry of this substituted N-bound urea complex and its protonated form. The latter ion rapidly isomerizes to the O-bonded urea complex, accompanied by a little competitive aquation, and the rate and course of this reaction afford a comparison with a number of other linkage isomerizations of this kind. Further, the kinetics and product analysis for the base hydrolysis of the dimethylurea-*O* isomer are reported for comparison with the data for the unsubstituted urea-*O* complex.[4a]

Finally, using variable-temperature ^{13}C and ^1H NMR and electronic spectra, we comment upon the solution structures of the precursor cyanamide complex and the N- and O-bonded urea complexes, most of which can exist in several canonical and/or tautomeric forms.

Experimental Section

Visible spectra (λ_λ^{max}, $M^{-1}\ cm^{-1}$) were recorded in duplicate with a Cary 14 spectrophotometer. ^1H NMR spectra were measured with a JEOL "Minimar" MH-100 or Varian T60 spectrometer at ~30 °C using Me_2SO-d_6 as solvent and sodium 4,4-dimethyl-4-silapentanesulfonate (DSS) or tetramethylsilane (Me_4Si) as references. Reported chemical shifts are downfield from DSS or Me_4Si as noted. Infrared spectra were recorded for KBr disks or Nujol mulls between KBr plates on JASCO IRA-2 or Perkin-Elmer 683 instruments. Measurements of pH were made under nitrogen at 25 °C with a Radiometer PHM 26 meter and GK2401B combination glass electrode standardized at two pH values as described by Bates.[12] All evaporations were carried out with Büchi rotary evaporators (<25 °C) under reduced pressure (~20 mmHg).

Solvents were reagent grade unless specified otherwise. Sulfolane was vacuum distilled from CaH_2 after drying by passage (<30 °C) through a column of molecular sieves. $[Co(NH_3)_5OSO_2CF_3](CF_3SO_3)_2$ was prepared as described.[8]

Syntheses. $[Co(NH_3)_5NCN(CH_3)_2](ClO_4)_3$. $[Co(NH_3)_5OSO_2CF_3](CF_3SO_3)_2$ (20 g) was added in small portions over 10 min to a stirring solution of dimethylcyanamide (10 g, Columbia Organic Chemicals Co.) in dry sulfolane (50 mL) or acetone (AR, 60 mL) at ~20 °C. The red solution, which changed to orange over 30 min and then solidified, was set aside at ~20 °C for 12 h. It was then stirred vigorously with diethyl ether (1 L) to give an orange suspension of the trifluoromethanesulfonate salt of the product. After filtration and thorough washing with ether, the residue was redissolved in a minimum volume of 2 mM CF_3SO_3H, filtered, and then cooled in an ice bath as solid $NaClO_4$ was added to crystallize the perchlorate salt. The analytically pure product, obtained after two recrystallizations from warm (~45 °C) water (200 mL) by addition of a little $HClO_4$ (~0.1 mL, 70% w/v) and cooling, was washed with ethanol and ether and dried in air (yield 9.2 g). The major impurity removed by recrystallization appeared to be $[Co(NH_3)_5OH_2](ClO_4)_3$ formed by aquation of $[Co(NH_3)_5OSO_2CF_3]^{2+}$ by traces of H_2O present in the commercial $NCN(CH_3)_2$. Anal. Calcd for $CoC_3H_{21}N_7O_{12}Cl_3$: Co, 11.50; C, 7.03; H, 4.13; N, 19.13; Cl, 20.75. Found: Co, 11.3; C, 7.3; H, 4.1; N, 19.1; Cl, 20.8. ^1H NMR (Me_2SO-d_6): δ 2.97 (6 H, s, CH_3), 3.20 (3 H, br s, trans NH_3), 3.67 (12 H, br s, *cis*-NH_3). Visible spectrum: $\epsilon^{max}{}_{486}$ 98.9, $\epsilon^{sh}{}_{345}$ 118.5 in 10^{-3} M $HClO_4$. The pure (chromatography) triflate salt was obtained also, by direct recrystallization of the crude product from a minimum volume of water with saturated aqueous $NaCF_3SO_3{\cdot}H_2O$[8] as the precipitant. Note that $[(NH_3)_5CoOH_2](CF_3SO_3)_3$ is more water soluble than the desired product. The crystals were washed with ethanol/ether (1:1) followed by ether and air-dried.

$[Co(NH_3)_5NHCON(CH_3)_2](CF_3SO_3)_2{\cdot}xH_2O$ ($x = 0,1$). To a stirred aqueous solution (1 L) of $[Co(NH_3)_5NCN(CH_3)_2](ClO_4)_3$ (8.5 g, 16.6 mmol) at ~20 °C was added an aqueous solution of LiOH (20 mL, 0.77 g, 18.2 mmol). After 20 min, the deep red solution was neutralized (pH 7, 1 M $HClO_4$). A little (~0.1 g) tris(hydroxymethyl)amin methane (Tris base) was added to give pH ~9, and then the solution was passed through a column (5 × 20 cm) of Dowex AG1-X4 (NO_3^- form) anion-exchange resin to remove ClO_4^-. After concentration of the eluant to 100 mL, ethanol (500 mL) was slowly added to give a precipitate of the nitrate salt of the product. After filtration and thorough washing with ethanol and ether, the residue was recrystallized from a cooled filtered solution 1 M in $LiNO_3$ (50 mL) by slow addition of ethanol. The solid residue after filtration and washing as above was redissolved in water (40 mL) and filtered. The solution deposited red crystals of the trifluoromethanesulfonate salt on slow addition of solid $NaCF_3SO_3{\cdot}H_2O$[8] and cooling. The product was collected by filtration, washed with ethanol/ether (20% v/v) and ether, and dried in vacuo over P_2O_5 (yield 6.0 g). It was consistently analyzed (Co, S, F) as the monohydrate but appeared to effloresce under the procedures used for sample preparation for automated C, H, N analysis. All concentrations were calculated by using the formula weight for the monohydrate. Anal. Calcd for $CoC_5H_{22}N_7O_7S_2F_6$: C, 11.35; H, 4.19; N, 18.52. Found: C, 11.3; H, 4.2; N, 18.4. Calcd for $CoC_5H_{22}N_7O_7S_2F_6{\cdot}H_2O$: Co, 10.77; S, 11.72; F, 20.83. Found: Co, 10.7; S, 11.4; F, 20.9. ^1H NMR (Me_2SO-d_6): δ 1.80 (1 H, br s, CoNH–), 2.80 (6 H, s, CH_3), 3.05 (3 H, br s, trans NH_3), 3.23 (12 H, br s, cis NH_3). Visible spectrum (0.1 M triethylamine hydrochloride, pH 11.9 (μ = 1.0 M, (KCl))): $\epsilon^{max}{}_{509}$ 110.9, $\epsilon^{sh}{}_{375}$ 219.

In preparations using impure $[Co(NH_3)_5NCN(CH_3)_2](ClO_4)_3$ as starting material, the perchlorate salt of the product was obtained directly from the reaction mixture by concentration and addition of solid $NaClO_4$. However, it was found by chromatography to contain an impurity of $[Co(NH_3)_5OH](ClO_4)_2$, which could not be removed by repeated recrystallization from warm 0.01 M Tris or from 0.01 M Tris/$NaClO_4$. By conversion of the ClO_4^- salt first to the NO_3^- salt and then to the $CF_3SO_3^-$ salt, the impurity was removed and the product proved to be analytically pure.

$[Co(NH_3)_5OC(NH_2)N(CH_3)_2]_2(S_2O_6)_3{\cdot}3H_2O$. Method 1. A filtered aqueous solution (50 mL) of $[Co(NH_3)_5NHCON(CH_3)_2](CF_3SO_3)_2{\cdot}H_2O$ (3.0 g) was titrated at ~20 °C to pH 2 and maintained thereat for 12 min by dropwise addition of 1 M HCl. The orange solution produced immediately on acidification rapidly turned to pink as the reaction proceeded. After neutralization (pH 6, 1 M NaOH), the solution was cooled to 0 °C as saturated aqueous $Na_2S_2O_6$ solution was slowly added. After 15 min, the intense pink needles were collected, washed with a little ice-cold water, ethanol, and ether and dried in vacuo over P_2O_5 (yield 2.5 g). Anal. Calcd for $Co_2C_6H_{46}N_{14}O_{20}S_6{\cdot}3H_2O$: Co, 11.80; C, 7.22; H, 5.25; N, 19.63; S, 19.26. Found: Co, 11.8; C, 7.2; H, 5.1; N, 20.0; S, 19.5. Visible spectrum (1 M $NaClO_4$): $\epsilon^{max}{}_{523}$ 93.5. The infrared spectrum (KBr disk, $\nu_{C=O}$ 1605, 1645 cm^{-1}) was very similar to that of $[Co(NH_3)_5OC(NH_2)_2]_2(S_2O_6)_3{\cdot}3H_2O$[4a,8] save for some weak absorptions assignable to the methyl substituents.

Method 2. *N,N*-Dimethylurea (5 g, Merck Chemicals) in acetone (50 mL) was dried over molecular sieves (4 Å, BDH) for 2 h. $[Co(NH_3)_5OSO_2CF_3](CF_3SO_3)_2$ (5 g) was then added, and the mixture was warmed (60 °C) for 10 min, cooled to room temperature, and then poured into diethyl ether (500 mL). After the mixture was

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stirred for 10 min and then settled, the ethereal layer was decanted and the residue again stirred with ether (200 mL). The pink residue was dissolved in a minimum of ice water and filtered into one-fifth volume of saturated aqueous $Na_2S_2O_6$. After the mixture was cooled (<5 °C) for 15 min, the pink crystals of $[Co(NH_3)_5OC(NH_2)N(CH_3)_2]_2(S_2O_6)_3\cdot 3H_2O$ were collected, washed with ice water, ethanol, and ether, and dried briefly in vacuo over P_2O_5; yield 3.8 g (86%).

The dithionate salt (0.5 g) suspended in ice-cold H_2O (5 mL) was converted to the perchlorate salt by slow addition of $HClO_4$ as described for the unsubstituted urea complex.[4a] ^1H NMR spectrum (Me_2SO-d_6): 2.67 (3 H, br s, trans NH_3), 2.74 (6 H, s, CH_3), 3.91 (12 H, br s, cis NH_3), 6.33 (2 H, br s, NH_2).

Kinetic Measurements. Buffers were prepared from reagent grade components and 1.00 M NaOH or 1.00 M HCl (Volucon) and were made up to $\mu = 1.0$ M with KCl. The kinetics of hydration of the $[Co(NH_3)_5NCN(CH_3)_2]^{3+}$ ion in NaOH/KCl ($\mu = 1.0$ M) solutions was followed spectrophotometrically at 380 nm. The N- to O-linkage isomerization of the $[Co(NH_3)_5NHCON(CH_3)_2]^{2+}$ ion in buffers and HCl or $HClO_4$ solutions was followed at 550 and 540 nm with a Cary 118C or 210 spectrophotometer. Equal volumes of solutions of the complex in water and buffer ($\mu = 2.0$ M, KCl) at twice the final concentration were mixed in a temperature-equilibrated stopped-flow reactor[13] fitted to a flow cell in the cell compartment of the spectrophotometer. The ensuing absorbance changes were monitored until a stable value was obtained. Temperatures were regulated to better than ±0.1 °C at 25 °C and to ±0.2 °C at other temperatures with use of jacketed silica cells; water was circulated from a Lauda thermostat bath.

The absorbance decrease at 540 or 550 nm that occurred on base hydrolysis of the $[Co(NH_3)_5OC(NH_2)N(CH_3)_2]^{3+}$ ion was followed with a Durrum-Gibson stopped-flow reactor (25 °C); data points were collected with a Biomation 805 waveform recorder. Apparent pH values of NaOH solutions ($\mu = 1.0$ M $NaClO_4$) were measured as previously described,[4a] and $[OH^-]$ was calculated from the relationships $K_w' = [H^+][OH^-] = 1.70 \times 10^{-14}$[14] and pH $= -\log [H^+]$.

Except where described in the Results section, all kinetic data obeyed strictly a first-order rate law (over $(3-4)t_{1/2}$). Progress curves were fitted by computer to a single exponential equation by standard least-squares procedures, giving values of the initial absorbance A_0 (and thence ϵ_0) and the first-order rate constant, k_{obsd}. Reported single values are the mean of three or more determinations under identical conditions. The electronic spectrum of the conjugate acid of the $[Co(NH_3)_5NHCON(CH_3)_2]^{2+}$ ion (in 0.5 M HCl, 0.5 M KCl) was determined similarly by following the kinetics of its isomerization at 25 °C at wavelengths (λ) of 5–10-nm intervals between 350 and 600 nm and plotting the computed values of ϵ_0 vs. λ (nm). At every wavelength, the computed value of k_{obsd} was $(1.7 \pm 0.1) \times 10^{-2}$ s^{-1}.

Later in this work, the complete absorption spectrum of the protonated N-bound isomer of the dimethylurea complex was obtained directly by rapidly and repetitively scanning (600–350 nm) solutions in 1.0 M $HClO_4$ at 2 °C and extrapolating the spectra to zero reaction time. The result (ϵ^{max}_{487} 69) agreed with that obtained at 25 °C as above.

Product Distributions. A sample of $[(NH_3)_5CoNCN(CH_3)_2](ClO_4)_3$ (0.1 g) was reacted in 0.10 M NaOH (10 mL) for $\geq 10t_{1/2}$ (30 s, 25 °C) and the electronic spectrum recorded (ϵ^{max}_{509} 111). The product mixture was diluted with water (300 mL) and sorbed on and eluted from SP-Sephadex C-25 (Na^+ form) cation-exchange resin using 0.1 M $NaClO_4$/0.1 M Tris (pH ~9) as eluent. A single pink 2+ ion was observed, $[(NH_3)_5CoNHCON(CH_3)_2]^{2+}$. In a separate experiment in which the product was eluted from Dowex 50W-X2 (Na^+ form, 200–400 mesh) cation-exchange resin with 1 M Na^+ (phosphate buffer, pH 7), a single pink 2+ ion was again observed. Since, under the latter conditions, $[(NH_3)_5CoOH]^{2+}$ elutes well behind the N-bound isomer, there appears to have been no competitive Co–N hydrolysis.

Samples of $[(NH_3)_5CoNHCON(CH_3)_2](ClO_4)_2$ were dissolved in 0.1 or 1.0 M $HClO_4$ at 25 °C. After $10t_{1/2}$ (~7 min), the products were diluted with ice water and sorbed on and eluted from SP-Sephadex C-25 (Na^+ form) cation-exchange resin in jacketed columns at ~2 °C. Elution with 0.5 M Na^+ (pH ~7, Cl^- (0.45 M)/HPO_4^{2-}/$H_2PO_4^-$ buffer) yielded a minor ($[(NH_3)_5CoOH_2]^{3+}$, 3%) followed by a major band ($[(NH_3)_5CoOC(NH_2)N(CH_3)_2]^{3+}$, 97%). Spectra of the eluates were measured immediately; [Co] was determined by using ϵ^{max}_{492} 50.5 for $[(NH_3)_5CoOH_2]^{3+}$ in this medium and ϵ^{max}_{523} 93.5 for $[(NH_3)_5CoOC(NH_2)N(CH_3)_2]^{3+}$. In the time taken for the chromatography (~1 h, 2 °C), aquation of the O-coordinated dimethylurea complex is negligible; the $[(NH_3)_5CoOH_2]^{3+}$ (3%) thus arose directly from the protonated urea-*N* complex. The chromatographic analysis for the two products (97:3) is consistent with the results from the kinetics of isomerization. The A_∞ values (at 550 and 540 nm) were reproducibly low by a few percent, indicating a little (~3%) $[(NH_3)_5CoOH_2]^{3+}$ was formed in parallel with the major dimethylurea-*O* product. In larger scale experiments (~1.0 g N-bonded dimethylurea complex), no yellow $[(NH_3)_6Co]^{3+}$, which elutes behind $[(NH_3)_5CoOH_2]^{3+}$ under the conditions above, was observed (<0.2%), indicating negligible CoN–C bond cleavage.

The products of the base hydrolysis of $[(NH_3)_5CoOC(NH_2)N(CH_3)_2]_2(S_2O_6)_3\cdot 3H_2O$ (in 0.1 M OH^-) were examined by ion-exchange chromatography as described previously[4a] for the unsubstituted urea-*O* complex. In duplicate experiments, the O-bonded dimethylurea complex (2.0 g) was reacted in 0.1 M OH^- for $\sim 20t_{1/2}$ (20 s, 25 °C) and then the reaction was quenched with 1 M $HClO_4$ or CH_3SO_3H to pH ~2–3. The product mixture was chromatographed on Dowex 50W-X2 resin (Na^+ form) with 1 M $NaClO_4$ (pH ~5) as eluent. Neither $[(NH_3)_5CoO_2C(NH_2)]^{2+}$ nor $[(NH_3)_5CoO_2C(N(CH_3)_2)]^{2+}$ was observed (<0.2%), signifying insignificant C–N cleavage. The major product was $[(NH_3)_5CoOH]^{2+}$, which was eluted by using 1 M $NaClO_4$ (pH ~11) and measured as $[(NH_3)_5CoOH_2]^{3+}$ (ϵ^{max}_{492} 47.7) after acidification with $HClO_4$ to pH ~2.

The chromatographic analyses were supported by isosbestic point data for the base-catalyzed hydration of $[(NH_3)_5CoNCN(CH_3)_2]^{3+}$ and N to O linkage isomerization of $[(NH_3)_5CoNH_2CON(CH_3)_2]^{3+}$ in acid solution. For the hydration reaction, sharp isosbestic points were apparent at 487 and 429 nm, which persisted for the entire reaction and corresponded exactly to the crossover points in the spectra of the reactant $[(NH_3)_5CoNCN(CH_3)_2]^{3+}$ and product $[(NH_3)_5CoNHCON(CH_3)_2]^{2+}$ ions. Similarly, sharp isosbestic points at 487 nm (ε 69.0) and 400 nm were observed for the reaction of $[(NH_3)_5CoNHCON(CH_3)_2]^{2+}$ in strong acid solution. Again, these were in close agreement with the crossover points in the spectra of $[(NH_3)_5CoNH_2CON(CH_3)_2]^{3+}$ and $[(NH_3)_5CoOC(NH_2)N(CH_3)_2]^{3+}$ ions. The product analysis of the isosbestic point data was not sufficiently sensitive to detect the small (~3%) amount of competitive hydrolysis (yielding $[(NH_3)_5CoOH_2]^{3+}$ and free ligand $NH_2CON(CH_3)_2$) established chromatographically.

^{13}C NMR and ^1H NMR Spectra. Fourier-transformed spectra were obtained at −20 to +35 °C on a JEOL 90FXQ instrument in the pulse mode, using an internal deuterium lock and dioxane as reference. All chemical shifts are relative to Me_4Si (0 ppm). Me_2CO-d_6, D_2O, and Me_2SO-d_6 were employed as solvents. The spectra of $[(NH_3)_5CoNHCON(CH_3)_2]^{2+}$ in acid solution were obtained with use of the perchlorate or the more soluble triflate salt. Slightly more (1.1–3.0 equiv) than the required amount of redistilled CF_3SO_3H (3M Co.) was chilled to <0 °C and added to the urea-*N* complex in Me_2CO-d_6 at −20 °C or D_2O at ~6 °C. Similar experiments were performed with CH_3SO_3H in place of CF_3SO_3H with equivalent results. The spectra were recorded immediately and were recorded at selected time intervals during the course of reaction.

Results

Hydration of the $[Co(NH_3)_5NCN(CH_3)_2]^{3+}$ Ion. Orange solutions of the [(dimethylcyanamide)pentaamminecobalt(III)]$^{3+}$ ion reacted rapidly under basic conditions to produce an intensely red product. This was identified by its isolation in good yield in preparative-scale experiments from similar reaction mixtures and by its characterization (see Discussion) as the N-coordinated deprotonated dimethylurea complex, $[Co(NH_3)_5NHCON(CH_3)_2]^{2+}$. The electronic absorption spectrum of the pure dimethylcyanamide complex after reaction in 0.01 M triethylamine hydrochloride buffer (pH 11.87, $\mu = 1.0$ M (KCl), 5 min) or 0.1 M NaOH (~3 s) was identical (±1%) to that of the $[Co(NH_3)_5NHCON(CH_3)_2]^{2+}$ ion recorded under the same conditions (Figure 1). Furthermore, ion-exchange chromatography (on SP-Sephadex

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[13] A device, modified to include thermostated reservoirs, similar to that described by: Inoue, Y.; Perrin, D. D. *J. Phys. Chem.* **1962**, *66*, 1689–1693.

[14] Harned, H. S.; Hamer, W. J. *J. Am. Chem. Soc.* **1933**, *55*, 2194–2206.

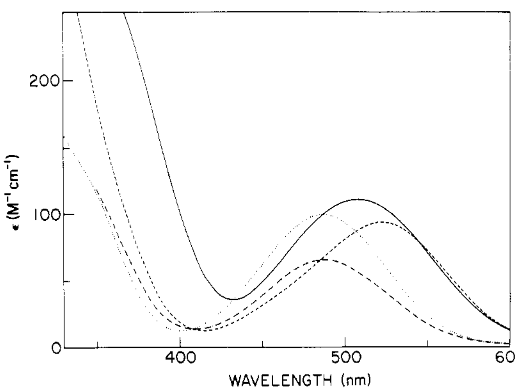

Figure 1. Electronic absorption spectra of $[Co(NH_3)_5NCN(CH_3)_2](ClO_4)_3$ in 10^{-3} M $HClO_4$ (···), of $[Co(NH_3)_5NHCON(CH_3)_2](CF_3SO_3)_2 \cdot H_2O$ in 0.10 M triethylamine hydrochloride buffer (μ = 1.0 M (KCl)) pH 11.9 (—) and in 0.5 M HCl, 0.5 M KCl (-·-·), derived as described in the text, and of $[Co(NH_3)_5OC(NH_2)N(CH_3)_2]_2(S_2O_6)_3 \cdot 3H_2O$ in 1.0 M $NaClO_4$ (- - -).

Table I. Kinetics of Reaction of the $[Co(NH_3)_5NCN(CH_3)_2]^{3+}$ Ion in Dilute NaOH Solutions (μ = 1.0 M (KCl)) at 25.0 °C[a]

$[OH^-]$, M	k_{obsd}, s^{-1} [b]	k_{OH}, M^{-1} s^{-1} [c]	$[OH^-]$, M	k_{obsd}, s^{-1} [b]	k_{OH}, M^{-1} s^{-1} [c]
0.01	0.0303	3.03	0.04	0.122	3.05
0.02	0.0610	3.05	0.08	0.248	3.10

[a] $[Co]_0 = 5 \times 10^{-4}$ M. [b] Observed first-order rate constant obtained from absorbance-time data for 380 or 390 nm. [c] $k_{OH} = k_{obsd}/[OH^-]$.

C-25 (pH 9) and Dowex 50W-X2 (pH 7)) of the reaction products showed the presence of a single red 2+ product; there was no competitive Co–N bond cleavage to yield $[(NH_3)_5CoOH]^{2+}$.

The kinetics of the reaction in dilute NaOH solutions (0.01–0.08 M, μ = 1.0 M, KCl), under conditions where $[OH^-] \gg [Co]$, followed strictly a first-order rate law. The first-order rate constants (k_{obsd}) were directly proportional to $[OH^-]$ (Table I), consistent with an overall rate law of the form of eq 1, where $k_{OH} = 3.06 \pm 0.03$ M^{-1} s^{-1} at 25 °C.

$$-d[Co]/dt = k_{OH}[OH^-][Co] \qquad k_{obsd} = k_{OH}[OH^-] \quad (1)$$

Isomerization of the $[Co(NH_3)_5(NH_2CON(CH_3)_2)]^{3+}$ Ion. The red deprotonated N-bound dimethylurea complex $[Co(NH_3)_5NHCON(CH_3)_2]^{2+}$ is indefinitely stable to reaction at pH 9, although it decomposes slowly with the ultimate formation of cobalt oxides under strongly basic conditions. Solutions changed color immediately to yellow on acidification and then underwent further reaction ($t_{1/2} \approx 40$ s in 0.1 M CF_3SO_3H, 25 °C) to produce a pink product. Within a day the pink solution faded to orange-red as the $[Co(NH_3)_5OH_2]^{3+}$ ion was ultimately produced. The pink product, formed initially, was identified by isolation (in >90% yield) and characterization (see Discussion) as the O-coordinated linkage isomer of the conjugate acid of the substrate, i.e. the $[Co(NH_3)_5OC(NH_2)N(CH_3)_2]^{3+}$ ion. A little competitive hydrolysis (3%) accompanied the linkage isomerization process, as established chromatographically. The immediately formed yellow species in acid solution is obviously the conjugate acid of the substrate, and this has been confirmed by a number of studies detailed below.

First-order rate constants for the isomerization of the N-bonded dimethylurea complex under acidic conditions (μ = 1.0 M (KCl)) at 25 °C (Table II)[15] varied with pH as a sigmoidal titration curve (Figure 2), consistent with a rate law of the form of eq 2. Least-squares fitting of k_{obsd}, $[H^+]$ data

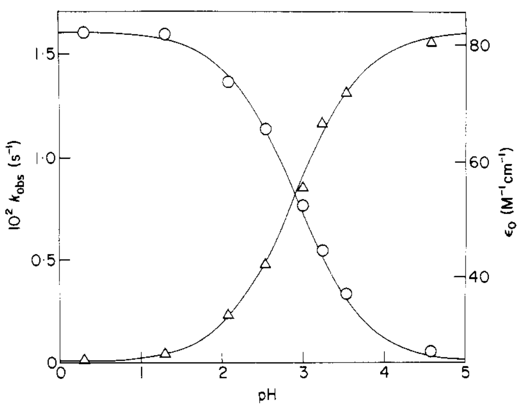

Figure 2. Dependence on pH of the first-order rate constant (○, left ordinate) and initial apparent molar absorption coefficient (△, right ordinate) for the isomerization of the $[Co(NH_3)_5NHCON(CH_3)_2]^{2+}$ ion under acidic conditions at 25.0 °C, μ = 1.0 M (KCl). Buffers used were 0.50 and 0.05 M HCl, 0.10 M glycine hydrochloride, pH 2.08, 2.54, and 2.99, and 0.10 M acetate, pH 3.24, 3.53, and 4.57. Solid curves were calculated from values of parameters given in the text and eq 2.

$$k_{obsd} = \frac{k[H^+]}{K_a' + [H^+]} \qquad (2)$$

to eq 2 gave values for the limiting first-order rate constant at acid pH; $k = (1.60 \pm 0.02) \times 10^{-2}$ s^{-1}, and the acid dissociation constant $K_a' = (1.19 \pm 0.07) \times 10^{-3}$ ($pK_a' = 2.92 \pm 0.03$) at 25 °C. At the highest pH studied (0.1 M acetate buffer, pH 4.57), the absorbance change during the isomerization reaction was very small. The A_{540} vs. time data showed an initial induction period followed by a slow decrease as the product O-bonded dimethylurea complex aquated. The data were analyzed by a least-squares computer fit to the sum of two exponential functions,[16] giving first-order rate constants for the isomerization reaction ($k_{obsd} = 5.6 \times 10^{-5}$ s^{-1}). In an independent experiment, the aquation of the $[Co(NH_3)_5OC(NH_2)N(CH_3)_2]^{3+}$ ion under the same conditions (pH 4.6, μ = 1.0 M (KCl), 25 °C) was observed strictly to follow a first-order rate law, $k_{aq} = 3.8 \times 10^{-5}$ s^{-1}. An average (three runs) value of $(3.05 \pm 0.1) \times 10^{-5}$ s^{-1} in 0.1 M $HClO_4$ (μ = 1.1 M ($NaClO_4$), 25 °C) was also determined.

From the kinetic data extrapolated by computer to $t = 0$ were also obtained values of ϵ_0, the apparent molar absorption coefficient at 540 nm ($\epsilon_0 = A_0/[Co]$) of the mixtures of $[Co(NH_3)_5NHCON(CH_3)_2]^{2+}$ (A^-) and its conjugate acid (HA) present at each value of pH. These data (Table II) also vary with pH, displaying a clean titration curve (Figure 2, line denoted by triangles). Computer fitting gave values of the limiting molar absorption coefficients ϵ_{HA} = 25.2 M^{-1} cm^{-1}, ϵ_{A^-} = 82.4 M^{-1} cm^{-1} and the acid dissociation constant $K_a' = (1.29 \pm 0.12) \times 10^{-3}$ ($pK_a' = 2.89 \pm 0.04$). The values of ϵ_{HA} and ϵ_{A^-} are in good agreement with those obtained from spectra of the substrate in 0.5 M HCl, 0.5 M KCl (Figure 1, ϵ_{540} = 25.5 M^{-1} cm^{-1}) and in 0.10 M triethylamine hydrochloride buffer (μ = 1.0 M (KCl)), pH 11.9 (Figure 1, ϵ_{540} = 83.3 M^{-1} cm^{-1}), while the consistency between the values of the pK_a' determined spectrophotometrically (2.89 ± 0.04) and kinetically (2.92 ± 0.03) demonstrates that the same ionization controls the two processes.

The kinetics of isomerization of the conjugate acid of the $[Co(NH_3)_5NHCON(CH_3)_2]^{2+}$ ion in 0.5 M HCl, 0.5 M KCl

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(15) Supplementary material.

(16) Jackson, W. G.; Harrowfield, J. M.; Vowles, P. D. *Int. J. Chem. Kinet.* **1977**, *9*, 535–548.

Table III. Temperature Dependence of the First-Order Rate Constant (k_{obsd}) for the Isomerization of the $[\mathrm{Co(NH_3)_5NH_2CON(CH_3)_2}]^{3+}$ Ion

temp, °C[a]	$10^2 k_{\mathrm{obsd}}$, $\mathrm{s^{-1}}$ [b]	temp, °C[a]	$10^2 k_{\mathrm{obsd}}$, $\mathrm{s^{-1}}$ [b]
	0.5 M HCl, 0.5 M KCl (μ = 1.0 M)[c,d]		
10.0	0.265 ± 0.004	32.0	3.40 ± 0.13
18.0	0.719 ± 0.010	40.0	7.99 ± 0.30
25.0	1.63 ± 0.01		
	0.1 M $\mathrm{HClO_4}$ (μ = 0.1 M)[e]		
35.5	5.88 ± 0.12	25.0	1.79 ± 0.05
29.4	2.99 ± 0.08	20.4	1.14 ± 0.04

[a] ±0.1 °C at 25.0 °C, up to ±0.2 °C at higher temperatures. [b] Observed first-order rate constant. [c] $[\mathrm{Co}]_0 = 4.8 \times 10^{-3}$ M. [d] $\Delta H^{\ddagger} = 80.9$ kJ/mol, $\Delta S^{\ddagger} = -7.7$ J/(deg mol), evaluated by weighted least-squares analysis of a plot of ln (k_{obsd}/T) vs. ($1/T$). [e] $\Delta H^{\ddagger} = 80.8 \pm 2.9$ kJ/mol, $\Delta S^{\ddagger} = -1.8 \pm 2.3$ J/(deg mol) (refer to footnote *d*).

and in 0.1 M $\mathrm{HClO_4}$ were also studied as a function of temperature (10–40 and 20–35 °C respectively, Table III). A plot of ln (k_{obsd}/T) vs. 1/T (not shown) was strictly linear, giving values of the activation parameters $\Delta H^{*} = 80.9$ kJ/mol and $\Delta S^{*} = -7.7$ J/(deg mol) for HCl/KCl (μ = 1.0 M) media and similar values for 0.1 M $\mathrm{HClO_4}$ (μ = 0.1 M, $\Delta H^{*} = 80.8 \pm 2.9$ kJ/mol, $\Delta S^{*} = -1.8 \pm 2.3$ J/(deg mol)).

Solution Structure and the Site of Protonation in $[\mathrm{Co(NH_3)_5(NH_2CON(CH_3)_2)}]^{3+}$. The electronic absorption spectrum of the $[\mathrm{Co(NH_3)_5NH_2CON(CH_3)_2}]^{3+}$ ion in 0.5 M HCl/0.5 M KCl (Figure 1), derived from the extrapolation of first-order kinetic plots obtained from data collected at suitable wavelengths (25 °C) and by direct observation (1 M $\mathrm{HClO_4}$) at low temperature (~2 °C) showed $\lambda^{\max}_{487}$ 69.0. This value of $\lambda_{\max}$ is to be contrasted with that for the deprotonated (2+) substrate), $\epsilon^{\max}_{509}$ 110.9 in 0.1 M triethylamine hydrochloride, pH 11.9. The change is as predicted for protonation of the substrate in comparison with those seen on deprotonation of Co(III) complexes of N-coordinated amides, sulfamate, cyanamide, amidines, and imines (see Discussion). The ^{1}H NMR spectrum of a red solution of the $[\mathrm{Co(NH_3)_5NHCON(CH_3)_2}]^{2+}$ ion in $\mathrm{Me_2SO}$-d_6 showed δ 1.80 (1 H, br s, CoNH–), 2.80 (6 H, s, $-\mathrm{CH_3}$), 3.05 (3 H, br s, trans $\mathrm{NH_3}$), and 3.23 (12 H, br s, cis $\mathrm{NH_3}$) from $\mathrm{Me_4Si}$. A spectrum of the orange solution recorded 10–110 s after addition of slightly greater than the stoichiometric amount of $\mathrm{H_2SO_4}$, $\mathrm{CF_3SO_3H}$, or $\mathrm{CH_3SO_3H}$ showed resonances at δ 2.94 (6 H, s, $\mathrm{NCH_3}$), 3.36 (3 H, br s, trans $\mathrm{NH_3}$), and 3.66 (12 H, br s, cis-$\mathrm{NH_3}$), which rapidly disappeared concomitantly with the ensuing color change to pink and the appearance of resonances assignable to the O-bonded dimethylurea complex at δ 2.74 (3 H, br s, trans $\mathrm{NH_3}$), 2.77 (6 H, s, $\mathrm{NCH_3}$), 3.96 (12 H, br s, cis $\mathrm{NH_3}$), and 6.46 (2 H, br s, $\mathrm{CONH_2}$). The broad signal in the region δ 7–8 (s, ≥2 H) shifted downfield, lost intensity, and sharpened considerably with time. The initial chemical shifts (and proton integrations) depended upon the [H$^+$]. The final spectrum (δ 0–6.5) was very similar to that of an authentic sample of $[\mathrm{Co(NH_3)_5OC(NH_2)N(CH_3)_2}](\mathrm{ClO_4})_3$ (see Experimental Section), save for traces of absorptions due to some (~3%) $[\mathrm{(NH_3)_5CoOS(CD_3)_2}]^{3+}$ and free ligand formed by solvolysis concurrently with the N to O linkage isomerization process.

Low-temperature ^{1}H NMR spectra were recorded for the N-bonded dimethylurea complex and its protonated form in $\mathrm{D_2O}$ and $\mathrm{Me_2CO}$-d_6 (Table IV). Table IV also includes some ^{1}H and ^{13}C NMR data for pentaamminecobalt(III) derivatives of cyanamides, amides, acetonitrile, carbamate, and cyanate (see Discussion).

Base Hydrolysis of the $[\mathrm{Co(NH_3)_5OC(NH_2)N(CH_3)_2}]^{3+}$ Ion. Like the unsubstituted O-bonded urea complex,[4a] the O-bonded [(dimethylurea)pentaamminecobalt(III)]$^{3+}$ ion is rapidly hydrolyzed in base with the production of $[\mathrm{Co(NH_3)_5OH}]^{2+}$ and free dimethylurea. There is no detectable hydrolysis of the ligand (to give the O-bonded carbamato complex). In 0.05–0.50 M NaOH (μ = 1.0 M, $\mathrm{NaClO_4}$), the reaction followed first-order kinetics (Table V).[15] As with the unsubstituted urea complex[4a] a plot of k_{obsd} vs. [OH$^-$] showed pronounced curvature (Figure 3) and is consistent with a similar rate law (eq 3).[4a,17] In the present case, $k_{\mathrm{s}} = 3.8 \times$

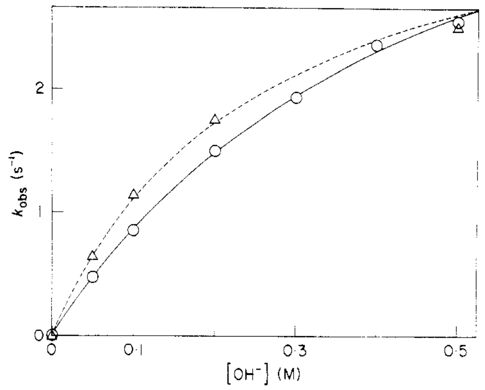

Figure 3. Variation with [OH$^-$] of the first-order rate constants (k_{obsd}) for the base hydrolyses of the $[\mathrm{Co(NH_3)_5OC(NH_2)_2}]^{3+}$ (△) and $[\mathrm{Co(NH_3)_5OC(NH_2)N(CH_3)_2}]^{3+}$ (○) ions at 25.0 °C, μ = 1.0 M ($\mathrm{NaClO_4}$). The curves were calculated from values of parameters given in the text and in ref 4a, according to eq 3.

$$k_{\mathrm{obsd}} = k_{\mathrm{s}} + \frac{K_{\mathrm{w}}' k_{\mathrm{OH}}}{K_{\mathrm{a}}' + [\mathrm{H^+}]} \tag{3}$$

10^{-5} s^{-1} (see above), $k_{\mathrm{OH}} = 10.33$ M^{-1} s^{-1}, and $K_{\mathrm{a}}' = 3.34 \times 10^{-14}$, where $K_{\mathrm{s}}' = 1.70 \times 10^{-14}$ (at 25 °C, μ = 1.0 M).

Discussion

Dimethylcyanamide, which contains both a nitrile and a tertiary amine as potential donor atoms, readily substituted for the labile $\mathrm{CF_3SO_3^-}$ group in the $[\mathrm{Co(NH_3)_5OSO_2CF_3}]^{2+}$ ion[8] to produce the orange (dimethylcyanamide)pentaamminecobalt(III) complex. This product was obtained as the analytically pure perchlorate and triflate salts after two recrystallizations. ^{1}H NMR spectroscopy and chromatography, for both the crude and the recrystallized products, indicated a single linkage isomer. The visible absorption (Figure 1) and ^{1}H NMR spectra are typical of an octahedral cobalt(III) complex containing six nitrogen donors.

The two linkage isomers of the unsubstituted cyanamide complex (I, III), unlike the dimethyl derivative, are also

$\mathrm{Co{-}N{\equiv}C{-}NH_2}$ I

$\mathrm{Co{-}NH{=}C{=}NH}$ II

$\mathrm{Co{-}NH_2{-}C{\equiv}N}$ III

tautomers and hence are readily interconverted by proton transfer. A third form (II) is also possible. The ^{1}H NMR spectrum indicates solution structure I or III for the $\mathrm{NH_2CN}$ complex, but the IR data (solid state) and the magnitude (10^5-fold) of the enhanced acidity of the $\mathrm{NH_2}$ protons on coordination are more consistent with I.[11] The $\mathrm{Me_2NCN}$ analogue can exist only in forms I or III, and in contrast, these forms should not be easily interconverted—the Co–N bond is not readily cleaved. Coordination via the bulky $\mathrm{Me_2N}$- donor is not expected, and moreover the IR data suggest

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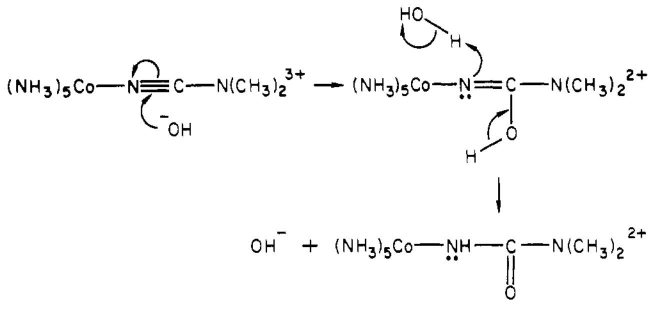
(17) It has been pointed out that (Stanbury, D., personal communication), strictly, eq 3 should read $k_{\mathrm{obsd}} = (k_{\mathrm{s}}[\mathrm{H^+}] + K_{\mathrm{w}}' k_{\mathrm{OH}})/(K_{\mathrm{a}}' + [\mathrm{H^+}])$, as should eq 1 of ref 4a. We are agreed that this is only a pedagogical distinction, since $k_{\mathrm{s}}[\mathrm{H^+}]/(K_{\mathrm{a}}' + [\mathrm{H^+}]) = k_{\mathrm{s}}$ to a very good approximation in the pH region where $K_{\mathrm{w}}' k_{\mathrm{OH}}$ is not $>> k_{\mathrm{s}}[\mathrm{H^+}]$.

bonding through the nitrile. The free ligand Me_2NCN shows a broad C–N stretch at 2190–2210 cm^{-1}, which is increased to 2280 cm^{-1} (sharp) on coordination. The corresponding frequencies for the H_2NCN system are 2210–2250 and 2310 cm^{-1}, respectively.[11] Thus, these data suggest at least the *same* mode of coordination for Me_2NCN and H_2NCN. The nitrile stretching frequency in $[(NH_3)_5CoNH_2CH_2CN]^{3+}$ is 2266–2275 cm^{-1} (broad),[11] and hence the cyanamide complexes could be argued to be nitrile bonded, but not strongly, on the basis of band shape.

The clearest evidence for nitrile coordination is the reaction of the dimethylcyanamide complex under basic conditions, which occurs on a time scale consistent with the Co—N≡C—R structure (vide infra).

In contrast to the unsubstituted cyanamide complex, which deprotonates in base to produce the stable intensely red carbodiimide complex,[11] the dimethylcyanamide complex initially retains its orange color. It does, however, react subsequently in NaOH solutions to produce a red product that has been identified as being the $[Co(NH_3)_5NHCON(CH_3)_2]^{2+}$ ion. At 25 °C and at constant ionic strength the reaction is first order in $[OH^-]$, $k_{OH} = 3.06\ M^{-1}\ s^{-1}$ (μ = 1.0 M (KCl), Table I). A mechanism consistent with both the production of $[Co(NH_3)_5NHCON(CH_3)_2]^{2+}$ and the rate law involves nucleophilic attack of OH^- on the nitrile carbon atom, followed by a proton transfer (eq 4).



(4)

Similar mechanisms have been proposed for the hydration of other Co(III)-coordinated nitriles. For example, $[Co(NH_3)_5NCCH_3]^{3+}$ reacts under basic conditions to produce the N-bonded acetamide complex.[10] The rate law for the base hydrolysis of the acetonitrile complex also has a term first order in $[OH^-]$, and the second-order rate constant (3.40 $M^{-1}\ s^{-1}$) is about (2×10^6)-fold greater than that for the corresponding reaction of free acetonitrile.[10]

There have been numerous studies on the activation of N-coordinated substituted nitriles toward base hydrolysis.[10,18,19] The present result (R = $N(CH_3)_2$, $k_{OH} = 3.0\ M^{-1}\ s^{-1}$) is remarkably similar to that for the acetonitrile complex (R = CH_3, $k_{OH} = 3.4\ M^{-1}\ s^{-1}$), suggesting that the lone pair on the N of the dimethylamine substituent does not participate through resonance in the ground or activated state for the base hydrolysis process, e.g.:

$$(NH_3)_5Co{-}N{\equiv}C{-}\ddot{N}(CH_3)_2{}^{3+} \nleftrightarrow (NH_3)_5Co{-}N^-{=}C{=}N^+(CH_3)_2{}^{3+}$$

However, other rate data for base-catalyzed hydration of $[(NH_3)_5M^{III}NCR]^{3+}$, while indicating a sensitivity to the nature of the metal ion,[10] show also a marked dependence on R (M = Co(III)).[10,18,19] This dependence of k_{OH} on R covers 7 orders of magnitude ($k_{OH} = 0.2\ M^{-1}\ s^{-1}$, *R* = $C_6H_5O^-$; $k_{OH} \approx 10^6$, R = C_6H_5CN), and the close agreement between k_{OH} values for R = CH_3 and R = $N(CH_3)_2$ could be regarded as fortuitous. Furthermore, a comparison of R_2N–CN and R_2NC–N bond lengths in cyanamides and RC–N bond lengths in simple nitriles reveals appreciable double-bond character for the R_2N–C bond,[20] indicating a significant contribution to the cyanamide structures from the canonical form IIa.

$$\underset{\text{Ia}}{R_2N{-}C{\equiv}N{:}} \longleftrightarrow \underset{\text{IIa}}{R_2N^+{=}C{=}^-\ddot{\underset{..}{N}}}$$

Presumably this e delocalization occurs also in the nitrile-bound Co(III) complex; IR data and the enhanced (~10^5-fold) acidity of the NH proton (R = H) on coordination[12] suggest this,[11] but there are no X-ray structural data to confirm it.

Further structural information comes from the ^1H and particularly the ^{13}C NMR spectra (Table IV). The nitrile carbons in the cyanamide (R = NH_2, $N(CH_3)_2$) complexes display very similar chemical shifts, indicating a common (Co—N≡C–) skeleton for the ground state. The deprotonated cyanamide complex $[(NH_3)_5Co{-}N{\equiv}C{-}\ddot{N}H]^{2+}$ shows the C resonance ~2 ppm further downfield from that for the parent ion $[(NH_3)_5Co{-}N{\equiv}C{-}NH_2]^{2+}$, and it is of interest to note the similar chemical shifts of the nitrile carbon for this carbodiimido ion and the isoelectronic isocyanato complex (Table IV). These observations, and the fact that both cations are inert to OH^- attack at the central carbon, are consistent with appreciable contributions from the structures

$$(NH_3)_5Co{-}\ddot{N}{=}C{=}\ddot{N}H \qquad (NH_3)_5Co{-}\ddot{N}{=}C{=}\ddot{\underset{..}{O}}$$

No reasonable structure for the other possible tautomer for the deprotonated cyanamide complex, $[(NH_3)_5CoNHCN]^{2+}$, consistent with the ^1H and particularly the ^{13}C NMR data (Table IV) can be drawn.

Attention is drawn to the rather striking difference in reactivity between the cyanamide complexes, $[(NH_3)_5CoNCNR_2]^{3+}$ (R = H, CH_3) and the isoelectronic (protonated) form of the isocyanate complex. The former are unreactive[11] while the latter hydrates extremely rapidly[21] to give (initially) the carbamato-*N* complex, $[(NH_3)_5CoNH_2COOH]^{3+}$. There is a corresponding contrast in reactivities for the free ligands.

The production of the deprotonated N-bound dimethylurea complex from the reaction between $[(NH_3)_5CoNCN(CH_3)_2]^{3+}$ and OH^- was confirmed by its isolation and characterization as the red trifluoromethanesulfonate salt. In Me_2SO-d_6, its ^1H NMR spectrum showed resonances due to the cis- and trans-NH_3 ligands separated by 0.12 ppm, a small difference typical for a complex with six nitrogen ligands.[11] The CoNH proton signal appeared at 1.80 ppm. The structure of the deprotonated N-coordinated dimethylurea complex is more likely $[(NH_3)_5CoNHCON(CH_3)_2]^{2+}$ rather than the alternative $[(NH_3)_5Co{-}N{=}C(OH)N(CH_3)_2]^{2+}$ tautomer. The high chemical shift for the isolated (single) proton in the ^1H NMR spectrum appears to be diagnostic of $Co\ddot{N}H$–. On the basis of a large number of observations for complexes of this type, Co—NH= and –OH type protons absorb at lower fields. Further, the decreased double-bond character for the coordinated imine in the deprotonated dimethylurea-*N* complex (δ 1.80), compared to that for its acetamide-*N* analogue (δ 3.72),[22] apparently results from the π-electron delocalization

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Table IV. Selected Carbon-13 and Proton NMR Data for Pentaamminecobalt(III) Complexes of Ureas, Cyanamides, Amides, Acetonitrile, Cyanate, and Carbamate

Carbon-13 NMR

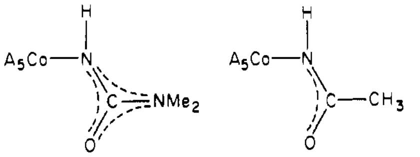
	assignt[a]				assignt[a]		
substance	δ(CN)	$\delta(NCH_3)$	$\delta(CCH_3)$	substance	δ(CN)	$\delta(NCH_3)$	$\delta(CCH_3)$
$(NH_3)_5CoNCO^{2+}$	127.34			$NH_2CON(CH_3)_2$	159.03	35.81	
$(NH_3)_5CoOC(O)NH_2{}^{2+}$	166.19			$(NH_3)_5CoOC(NH_2)N(CH_3)_2{}^{3+}$	162.20	36.76	
$(NH_3)_5CoNCN(CH_3)_2{}^{3+}$	125.82	39.17		$(NH_3)_5CoNHCON(CH_3)_2{}^{2+}$	166.46	36.52	
$(NH_3)_5CoNCNH_2{}^{3+}$	124.44				182.89[b]	14.98[b]	
$(NH_3)_5CoNCNH^{2+}$	126.31			$(NH_3)_5CoNH_2CON(CH_3)_2{}^{3+}$	*b,c*	14.63[b]	
$(NH_3)_5CoNCCH_3{}^{3+}$	130.81		3.77	$N(CH_3)_2CHO$	162.20	35.60, 30.59	
$NCCH_3$	117.7		1.30	$(NH_3)_5CoOCHN(CH_3)_2{}^{3+}$	167.57	38.50, 32.70	
NH_2CONH_2	160.69			$N(CH_3)_2COCH_3$	169.46	37.20, 34.22	21.08
$(NH_3)_5CoOC(NH_2)_2{}^{3+}$	165.83			$(NH_3)_5CoOC(CH_3)N(CH_3)_2{}^{3+}$	175.80	38.85, 36.65	19.29

Proton NMR

	assignt[a]					
substance	δ(cis NH_3)	δ(trans NH_3)	δ(NH)	$\delta(NCH_3)$	$\delta(CCH_3)$	δ(OCH)
NH_2CONH_2			5.62			
$(NH_3)_5CoOC(NH_2)_2{}^{3+}$	3.90	2.50	6.62			
$NH_2CON(CH_3)_2$			5.73	2.80		
$(NH_3)_5CoOC(NH_2)N(CH_3)_2{}^{3+}$	3.91	2.67	6.33	2.74		
	4.33[d]	3.03[d]	6.18[d]	2.93[d]		
	4.65[e]		7.70[e]	3.12,[e] 3.18[e]		
	4.16[f]			2.87[f]		
$(NH_3)_5CoNHCON(CH_3)_2{}^{2+}$	3.23	3.05	1.80	2.80		
	3.64[b]	3.51[b]	1.95[b]	2.90[b]		
	3.72[e]	3.60[e]	2.13[e]	2.89[e]		
$(NH_3)_5CoNH_2CON(CH_3)_2{}^{3+}$	3.72	3.39		2.97		
	4.17[b]	3.80[b]		3.23, 3.02[b]		
	4.19[e]	3.83[e]		3.22, 3.02[e]		
	3.85[f]			3.02[f]		
$N(CH_3)_2CHO$				2.90, 2.73		7.83
$(NH_3)_5CoOCHN(CH_3)_2{}^{3+}$	3.80	2.70		3.03, 2.85		7.36
$N(CH_3)_2COCH_3$				2.87, 2.72	1.92	
$(NH_3)_5CoOC(CH_3)N(CH_3)_2{}^{3+}$	3.90	2.60		2.98, 2.78	1.87	

[a] Downfield from Me_4Si. The solvent is Me_2SO-d_6 (30 °C) unless specified otherwise. Typical [Co] = 0.2 g/1.5 mL (perchlorate salts). [b] Acetone-d_6 solvent, −10 °C; Me_4Si reference. [c] Carbonyl resonance not clearly observed because of significant N to O linkage iosmerization during accumulation time. [d] Acetone-d_6 solvent, 30 °C; Me_4Si reference. [e] Acetone-d_6 solvent, −20 °C; Me_4Si reference. [f] D_2O solvent, 5 °C; DSS reference.

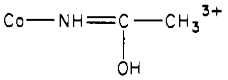
about the NMe_2 substituent, in addition to delocalization about the (common) carbonyl group:



However, ambient- and even low-temperature (−20 °C) ^1H and ^{13}C NMR data (Table IV) indicate that the rotation about the exo-C⩦N bond in the dimethylurea-*N* complex is not sufficiently restricted to render the *gem*-methyl groups diastereotopic. This is also true of the free urea ligands; N substituents are chemically equivalent in the NMR spectra, yet X-ray structural data[20] indicate undoubted π-electron delocalization about the C–O and both C–N bonds in these flat molecules.

On treatment with acid, the dimethylurea-*N* complex protonates to produce its yellow conjugate acid. The pK_a' of the N-coordinated [(dimethylurea)pentaamminecobalt(III)]$^{3+}$ ion (2.9) is comparable with that of the corresponding N-coordinate acetamide complex (3.1).[10] Since the latter protonates at the carbonyl oxygen when coordinated to cobalt(III)[10,22] and linkage isomerizes to the O-bound form comparatively slowly,[22] it is pertinent to examine evidence for the alternative sites of protonation (N or O) of the dimethylurea complex.

The deprotonated N-bound acetamide complex has been shown to protonate in Me_2SO soluton to yield the tautomer of the form[10,22]



$$Co{-}NH{=}\underset{\displaystyle OH}{\underset{|}{C}}{-}CH_3{}^{3+}$$

The compelling evidence rests with the observation of the NH singlet in the ^1H NMR spectrum which gives an integration for one proton and displays a chemical shift and intensity independent of excess H^+. Since the original work,[10] this yellow protonated form has been isolated in a pure state and the chemical shift of the acidic OH proton located (δ 10.00, 1 H, Me_2SO-d_6).[22] The OH proton readily exchanges with added H_2O and H^+ in Me_2SO, on the NMR time scale, giving rise to a singlet. The chemical shift and intensity are dependent upon the relative concentrations of the protonated acetamide-*N* complex and introduced H^+ and H_2O. This situation is similar to that found for the uncoordinated amide, which also protonates on the oxygen atom.[23] It is also relevant to note that the isoelectronic amidine Co(III) complexes appear to favor the tautomer in which the proton resides on the exo nitrogen, i.e. $[CoNH{=}C(R){-}NH_2]^{n+}$ rather than $[CoNH_2{-}C(R){=}NH]^{n+}$.[24]

Despite the reactivity of the dimethylurea-*N* complex, we were able to record the ^1H NMR spectrum of its protonated

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(22) Fairlie, D. P.; Jackson, W. G., unpublished data.

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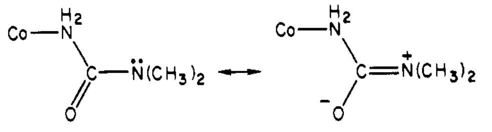
form in Me_2SO-d_6. No clear NH single was observed corresponding to O protonation. Instead, a broad singlet of variable intensity (>2 H) and chemical shift (δ 7–8) was noted. The interpretation is not unequivocal, but this result is consistent with the N-protonated $[(NH_3)_5CoNH_2CON(CH_3)_2]^{3+}$ species where the NH_2 protons are in rapid (NMR time scale) exchange with free H^+.

Because of rapid H–D exchange, a similar experiment cannot be performed in D_2O. Nonetheless, it seems likely that the complex is N protonated in aqueous media. This is supported by the similar visible spectra and N- to O-isomerization rates in the Me_2SO and H_2O solvent systems.[22]

The low-temperature ^1H NMR spectra in Me_2CO-d_6 and D_2O provide further information on solution structure (Table IV). Of special note is the observation of diastereotopic methyl groups for the ^1H NMR spectrum of the $[(NH_3)_5CoNH_2CON(CH_3)_2]^{3+}$ ion in Me_2CO-d_6 at <–10 °C. The methyl groups appear as a singlet in Me_2CO-d_6, D_2O, and Me_2SO-d_6 above 0 °C. The former observation indicates that rotation about the $C\overset{\cdot\cdot}{-}N(CH_3)_2$ bond is restricted due to appreciable C–N double-bond character. Thus there is a significant contribution to the structure from the canonical form **B**.

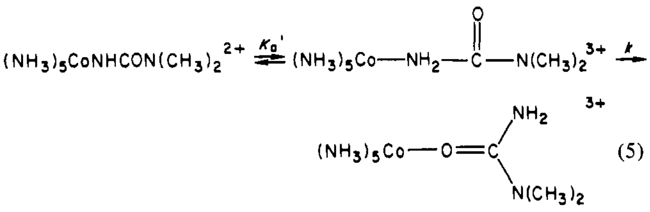


A B

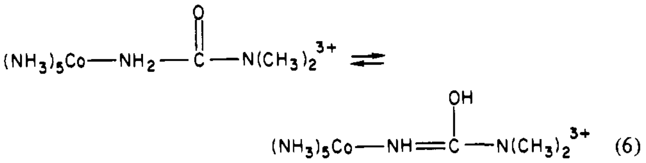
The recently prepared unsubstituted N-bonded urea complex $[(NH_3)_5CoNH_2CONH_2]^{3+}$ shows separate resonances (2:1:1 intensity ratio) for all the NH protons in Me_2SO-d_6, even at 35 °C.[22] Again, appreciable restricted rotation about the exo-C–N bond is implied. Also, this result establishes clearly the site of protonation, on nitrogen.

Under acidic conditions, the N-coordinated [(dimethylurea)pentaamminecobalt(III)]$^{3+}$ ion isomerizes to the O-coordinated isomer. The product was isolated and characterized as the sesquihydrate of its dithionate salt. In crystallization with this stoichiometry as sparingly soluble pink needles, and in respect to its ^1H NMR, infrared, and visible spectra, its properties closely resemble those of the $[Co(NH_3)_5OC(NH_2)_2]^{3+}$ and $[Rh(NH_3)_5OC(NH_2)_2]^{3+}$ ions.[4,8] Its ^1H NMR spectrum in Me_2SO-d_6 shows resonances due to the trans- and cis-ammine protons at δ 2.67 and 3.91, separated to an extent typical of a $(NH_3)_5Co^{III}$ complex containing an oxygen donor ligand.[11] The urea $-NH_2$ protons appear at 6.33 ppm. The corresponding values for the $[Co(NH_3)_5OC(NH_2)_2]^{3+}$ ion are δ 2.50, 3.90, and 6.62, respectively.[4b]

The rate law for isomerization is consistent with the mechanism of eq 5, in which only the protonated form of the N-coordinated substrate is reactive, and this isomerizes in a reaction that shows no dependence on $[H^+]$. As argued above, the available NMR evidence suggests that the acid form of the substrate is protonated predominantly, if not entirely, at the donor nitrogen atom rather than at the remote carbonyl oxygen. Nevertheless, a rapid equilibrium (eq 6) between the two forms must exist, but the N-protonated form would appear to be more disposed toward a facile N- to O-isomerization reaction. However, other work[22] indicates that factors additional to the proximity to the Co(III) center of the incoming nucleophile are apparently important in the linkage isomerization process. The large difference in reactivity between the protonated dimethylurea-N ($t_{1/2}$ = 40 s, 25 °C) and acetamide-N ($t_{1/2} \approx$ 16 h, 25 °C[22]) complexes implicates the protonation site as important. The dominant factor may be the propensity of the dimethylurea-N complex to more readily adopt a π-bonded transition state (or intermediate), similar to that proposed for the O- to O′- and O- to N-isomerization reactions of the $[(NH_3)_5CoONO]^{2+}$ complex,[25] and at this time the controlling factors in this rearrangement are unclear.



$$(NH_3)_5CoNHCON(CH_3)_2^{2+} \overset{K_a'}{\rightleftharpoons} (NH_3)_5Co-NH_2-\overset{\overset{\displaystyle O}{\|}}{C}-N(CH_3)_2^{3+} \xrightarrow{k} (NH_3)_5Co-O=C\begin{matrix}NH_2\\ N(CH_3)_2\end{matrix}{}^{3+} \tag{5}$$



$$(NH_3)_5Co-NH_2-\overset{\overset{\displaystyle O}{\|}}{C}-N(CH_3)_2^{3+} \rightleftharpoons (NH_3)_5Co-NH=\overset{\overset{\displaystyle OH}{|}}{C}-N(CH_3)_2^{3+} \tag{6}$$

The temperature dependence of the isomerization rate constant (k, Table III) gives values of $\Delta H^\ddagger$ and $\Delta S^\ddagger$ of 80.9 kJ/mol and –7.7 J/(deg mol), respectively (μ = 1.0 M). Similar values were found at lower ionic strength (μ = 0.1 M, $\Delta H^\ddagger$ = 80.8 ± 2.9 kJ/mol, $\Delta S^\ddagger$ = –1.8 ± 2.3 J/(deg mol)). These may be compared with values of the same parameters observed for other linkage isomerizations at Co(III) centers: $[(NH_3)_5CoONO]^{2+} \rightarrow [(NH_3)_5CoNO_2]^{2+}$ ($\Delta H^\ddagger$ = 95 ± 4 kJ/mol, $\Delta S^\ddagger$ = –4 ± 12 J/(deg mol), μ = 1.0 M[25]; $\Delta H^\ddagger$ = 91.6 ± 0.8 kJ/mol, $\Delta S^\ddagger$ = –17 ± 3 J/(deg mol), μ = 0.1 M[26]); $[(NH_3)_5CoSCN]^{2+} \rightarrow [(NH_3)_5CoNCS]^{2+}$ ($\Delta H^\ddagger$ = 102.8 ± 0.8 kJ/mol, $\Delta S^\ddagger$ = –14 ± 3 J/(deg mol), μ = 0.1 M[27]); $[(NH_3)_5CoNH_2SO_3]^{2+} \rightleftharpoons [(NH_3)_5CoOSO_2NH_2]^{2+}$ ($\Delta H^\ddagger$ = 103 kJ/mol, $\Delta S^\ddagger$ = 46 J/(deg mol), μ = 1.0 M[28]). At this time, there appears to be no obvious correlation between values of these parameters and the nature of the linkage isomerization process. For the nitrito → nitro system at least, the rate constants and both activation parameters are strongly solvent dependent and this has been discussed in detail.[29]

In our earlier study of the base hydrolysis of the $[(NH_3)_5CoOC(NH_2)_2]^{3+}$ ion,[4a] we found that it hydrolyzed predominantly with cobalt–oxygen bond rupture by an S_N1CB mechanism to produce $[(NH_3)_5CoOH]^{2+}$. The coordinated urea deprotonated to an appreciable degree at high pH (pK_a' = 13.2) to produce its conjugate base, and this accounted for curvature of a plot of k_{obsd} vs. $[OH^-]$ (Figure 3) at [OH–] = 0.05–0.50 M.[4a] Curvature of the analogous plot for the hydrolysis of the $[(NH_3)_5CoOC(NH_2)N(CH_3)_2]^{3+}$ ion in the present study (Figure 3) is less marked and indicates a somewhat higher pK_a' (13.48) for the coordinated dimethylurea. This difference between the two complexes is completely accounted for by the statistical effect of the unsubstituted urea complex having twice as many dissociable protons. We note that the structurally similar O-coordinated sulfamate complex $[(NH_3)_5CoO_3S(NH_2)]^{2+}$ has a pK_a' 13.1, μ = 1.0 M, 25 °C) similar to that of the O-coordinated urea complex. This value was also derived from significant curvature in plots of k_{obsd} vs. $[OH^-]$ for base hydrolysis,[28] and the deprotonated $[(NH_3)_5CoO_3SNH]^{2+}$ ion also appeared to be relatively unreactive toward OH^-.

It is important to point out that in neither the previous urea[4a] nor the present dimethylurea base hydrolysis study is the

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reactive entity identified. The form of the rate law is identical whether it be the conventional conjugate base $[(NH_3)_4(NH_2)CoOC(NH_2)NR_2]^{2+}$ and/or its tautomer $[(NH_3)_5CoOC(NH)NR_2]^{2+}$ (R = H, CH_3). The approach of a limiting rate at high $[OH^-]$ merely establishes an appreciably greater relative concentration of the latter species, since the pK_a' for the former is undoubtedly >14. However, with use of the measured values of k_{OH} (10.3 M^{-1} s^{-1}) and pK_a' (13.5) and the assumption of a pK_a' of 15 for deprotonation of coordinated NH_3, a specific rate of ~1 s^{-1} can be calculated for $[(NH_3)_5CoOC(NH)NR]^{2+}$ and ~100 s^{-1} for $[(NH_3)_4(NH_2)CoOC(NH_2)NR_2]^{2+}$. The latter value is typical, whereas the former implies an unusually high reactivity for a pentaamminecobalt(III) species, especially as the leaving group is an anion, NR_2CONH^-.

The dimethylurea complex is similar in reactivity to the $[(NH_3)_5CoOC(NH_2)_2]^{3+}$ ion[4a] in respect to both spontaneous ($k_s = 3.8 \times 10^{-5}$ (cf. 5.1×10^{-5}) s^{-1}) and base-catalyzed (k_{OH} = 10.3 (cf. 15.3) M^{-1} s^{-1}) aquation. There is a small but real difference in the values of k_s determined for the neutral-pH region (~5), after subtracting from k_{obsd} the contribution from the base-catalyzed pathway, and the values of k_s determined by direct measurement in 0.1 or 1.0 M $HClO_4$ (μ = 1.0 M). For the urea-*O* complex, $k_s = 3.9 \times 10^{-5}$ s^{-1} in $HClO_4$ (cf. 5.1×10^{-5} [4a]), and for the dimethylurea-*O* complex, $k_s = 3.1 \times 10^{-5}$ s^{-1} (*cf.* 3.8×10^{-5} s^{-1}). The significance of these differences is discussed elsewhere.[4c]

A small fraction (2.5%) of base hydrolysis of the unsubstituted urea complex in $^{18}OH_2$ occurred by way of nucleophilic attack of OH^- at the coordinated carbonyl to produce the intermediate $[(NH_3)_5CoOC(^{18}OH)NH_2)_2]^{2+}$ ion. This species collapsed preferentially with carbon–oxygen cleavage (yielding $[(NH_3)_5CoOH]^{2+}$ and (^{18}O)urea) rather than by way of carbon–nitrogen cleavage to give the $[(NH_3)_5CoO_2CNH_2]^{2+}$ ion and free NH_3.[4a] No ^{18}O-tracer studies of the base hydrolysis of the dimethylurea complex have been carried out, and although we would anticipate that a similar situation obtains, anion competition studies[30,31] indicate negligible carbon–oxygen bond fission.

In conclusion, some comment on the efficacy of attack of OH^- at the carbonyl centers of O-coordinated ureas ($OC(NH_2)NR_2$; R = H, CH_3) and amides ($OC(H)NR_2$; R = H, CH_3) is appropriate. Relevant ^1H and ^{13}C NMR data are recorded in Table IV. As for the deprotonated N-bound dimethylurea complex, neither of the O-coordinated urea complexes provide direct ^1H or ^{13}C NMR evidence at 30–35 °C for restricted rotation about the exo-$C\overset{\cdot\cdot}{-}N$ bond in contrast to, e.g. the amide-*O* complex ion $[(NH_3)_5CoOCHN(CH_3)_2]^{3+}$.[22,32] At least on the NMR time scale at these temperatures, the *gem*-NH_2 and -$N(CH_3)_2$ protons are equivalent. The $N(CH_3)_2$ groups appear as a singlet in the ^{13}C (and ^1H) NMR spectra (in Me_2SO-d_6, Me_2CO-d_6, and D_2O). This is also true of the free urea ligands.[4c,33] However, we have detected restricted rotation in the oxygen-bonded dimethylurea complex in the low-temperature ^1H NMR spectrum (Table IV) but not in the free ligand. Thus, it does appear that O coordination increases the double-bond character of the C–N bonds of these (flat) urea ligands. Also, the downfield shifts for the NR_2 signals in the ^1H and ^{13}C NMR spectra indicate some polarization by O coordination to cobalt(III). Moreover, the carbonyl ^{13}C resonance is shifted 3–5 ppm downfield on coordination. Further discussion on the significance of these observations is deferred to a later publication concerned with a range of substituted N- and O-bonded urea and amide complexes, but we note that the NMR spectra of the complexes are consistent with their other properties discussed previously.[34]

The analogous O-coordinated amide complexes, $[(NH_3)_5CoOCRNH_2]^{3+}$ and $[(NH_3)_5CoOCRN(CH_3)_2]^{3+}$ [22,32] (R = CH_3, H), show separate resonances for the $-NH_2$ and $-N(CH_3)_2$ protons in the ^1H NMR spectra, even at 35 °C (Me_2SO-d_6), and for the methyl carbons of the dimethylformamide and dimethylacetamide complexes in the ^{13}C NMR spectra at 30 °C. This is also true of the free amide ligands (Table IV). Superficially, these results imply more double-bond character in the exo-C–N bond in these amide complexes. Consistent with this interpretation, these complexes appear to be more sensitive to attack by OH^- *at the ligand*, readily yielding $(NH_3)_5CoO_2CR^{2+} + R'_2NH$ under conditions where the corresponding urea derivatives are unreactive.[34] However, we recognize that the urea-*O* complexes base hydrolyze with Co–O cleave more rapidly than the $[(NH_3)_5CoOCHNRR']^{3+}$ ions[4a,22,32] and that OH^- attack at the carbonyl center does not lead necessarily to C–N cleavage,[4a,32] and detailed rate and ^{18}O-tracer studies are required to resolve this issue unequivocally.

Acknowledgment. We thank the Microanalytical Section, The Australian National University, for elemental analysis.

Registry No. $[(NH_3)_5CONCN(CH_3)_2]^{3+}$, 87450-94-0; $[(NH_3)_5CoNHCON(CH_3)_2]^{2+}$, 87450-95-1; $[(NH_3)_5CoOC(NH_2)N(CH_3)_2]^{3+}$, 84623-21-2; Co, 7440-48-4.

Supplementary Material Available: Kinetic data (Tables II and V) (2 pages). Ordering information is given on any current masthead page.

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