Reversible Linkage Isomerization of Pentaamminecobalt(III) Complexes of Urea and its *N*-Methyl Derivatives

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Abstract

The $(NH_3)_5CoOC(NH_2)_2^{3+}$ ion is consumed in water according to the rate law $k(obs.) = k_1 + k_2[OH^-]$, where $k_1 = 4.0 \times 10^{-5}$ s^{-1} and $k_2 = 14.2$ M^{-1} s^{-1} (0–0.1 M $[OH^-]$; μ = 1.1 M, $NaClO_4$, 25 °C). A hitherto unrecognized intramolecular O- to N-linkage isomerization reaction has been detected. In strongly acid solution only aquation to $(NH_3)_5Co\text{-}OH_2^{3+}$ is observed, but in 0.1–1.0 M $[OH^-]$, 7% of the directly formed products is the urea-*N* complex $(NH_3)_5CoNHCONH_2^{2+}$ which has been isolated. In the neutral pH region a much greater proportion (25%) of the products is the urea-*N* species. These results are interpreted in terms of an urea-*O* to urea-*N* linkage isomerization reaction competing with hydrolysis for both spontaneous (k_1) and base-catalyzed (k_2) pathways; the rearrangement is not observed in strongly acidic solution (pH $\leq$ 1) because the protonated N-bonded isomer ($pK'_a \sim 3$) is unstable with respect to the O-bonded form. The appearance of the isomerization pathway as the pH is raised in the 0–6 region is commensurate with a rate increase which cannot be attributed to a contribution from the base catalysis term $k_2[OH^-]$. It is argued that this observation establishes, for the spontaneous pathway, that hydrolysis and linkage isomerization are separate reaction pathways – there is no common intermediate. The product distribution and rate data lead to the complete rate law, $k(obs.) = k_1 + k_2[OH^-] = (k_s + k_{ON}) + (k_{OH} + k'_{ON})[OH^-]$ for the reactions of the O-bonded isomers, where k_s, k_{OH} are the specific rates for hydrolysis, and k_{ON}, k'_{ON} are the specific rates for O- to N-linkage isomerization, by spontaneous and base-catalyzed pathways respectively; $k_{ON} = 1.3 \times 10^{-5}$ s^{-1} and $k'_{ON} = 1.1$ M^{-1} s^{-1} (μ = 1.0 M, $NaClO_4$, 25 °C). The O- to N-linkage isomerization has been observed also for complexes of *N*-methylurea, *N,N*-dimethylurea and *N*-phenylurea, but not for the *N,N'*-dimethylurea species. There is an approximately statistical relationship among the data for $-NH_2$ capture (*versus* H_2O), while $-NHR$ and $-NR_2$ do not compete with water as nucleophiles for Co(III) in either the spontaneous or base-catalyzed hydrolysis processes. For each urea-*O* complex, O- to N-isomerization is a more significant parallel reaction in the spontaneous as opposed to the base-catalyzed pathway. This is interpreted as being indicative of more associative character in the spontaneous route to products, a conclusion supported by other evidence. Some activation parameter data have been recorded and the effect of the N-substitution on the rates of solvolysis (H_2O, Me_2SO) is discussed. The urea-*N* complexes have been isolated as their deprotonated forms, $[(NH_3)_5CoNHCONRR'](ClO_4)_2 \cdot xH_2O$ (R,R' = H, CH_3). They are kinetically inert in neutral to basic solution but in acid they protonate (H_2O, pK'_a 2–3; μ = 1.0 M, 25 °C) and then isomerize rapidly back to their O-bonded forms. Some solvolysis accompanies this N- to O-rearrangement in H_2O and Me_2SO. Specific rates and activation parameters are reported. The kinetic data follow a rate law of the form $k_{NO}(obs.) = (k + k_{NO})[H^+]/(K'_a + [H^+])$ and the active species in the reaction is the protonated form; k, k_{NO} are the specific rates for hydrolysis and isomerization, respectively. Proton NMR data establish that the site of protonation (in Me_2SO) is the cobalt-bound nitrogen atom. For the unsubstituted urea species $(NH_3)_5CoNH_2CONH_2^{3+}$, diastereotopic *exo*-$NH_2$ protons arising from restricted rotation about the C=N bond are observed. The relevance to the mechanism of the linkage isomerization process is considered. ^{13}C and ^1H NMR and electronic absorption spectral data are presented, and distinctions between linkage isomers and the solution structures (electronic and conformational) are discussed. The urea-*N*/urea-*O* complex equilibrium is governed by the relation $K'_{NO}(obs.) = K'_{NO}[H^+]/([H^+] + K'_a)$, where K'_{NO} is the equilibrium constant = $[(NH_3)_5Co(urea\text{-}O)^{3+}]/[(NH_3)_5Co(urea\text{-}N)^{3+}]$. Values for K'_{NO} ($= k_{NO}/k_{ON}$) = 260 and $pK'_a \sim 3$ for the NH_2CONH_2 system are consistent with the stability of the N-isomer in feebly acidic to basic solution (e.g. pH 6, $K'_{NO}(obs.) = 2.6 \times 10^{-2}$) and

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instability in acid solution (e.g. pH 1, K'_{NO}(obs.) = 240). The equilibrium data for this and other urea complexes of $(NH_3)_5Co(III)$ are contrasted with the result for the analogous Rh(III)–NH_2CONH_2 system ($K'_{NO} \sim 1$).

Introduction

Studies on the phenomenon of linkage isomerism in transition metal complexes containing ambidentate ligands have often been confined to descriptions of the synthesis of the particular isomers. Moreover, in many cases only one of the possible linkage isomers has been isolated [1]. Nonetheless, in instances where more than one form is known, the isomers have often been shown to interconvert, but there have been few studies designed to probe the detailed mechanism of these rearrangements. The S- and N-bonded NCS^- and N- and O-bonded NO_2^- aminecobalt(III) systems are notable exceptions [2–5].

New kinds of linkage rearrangements on Co(III) have recently emerged from our own and other laboratories, e.g., O- to S-bonded $S_2O_3^{2-}$ [6] and SO_3^{2-} [7, 8], ^{17}O- or ^{18}O-scrambling in O-bonded NO_2^- [9] and $CH_3CO_2^-$ complexes [10], S- to O-bonding in a sulfoxide [11] and an alkane sulfinylchloride [1], O- to F-bonded FSO_3^- [12] and O- to S-bonding in alkanesulfinates [13], to name a few. Furthermore, some of these reactions have been shown to be base- and metal-ion-catalyzed as well as photochemically induced [1].

This article describes a detailed study of the solution structure and reactions of O- and N-bonded urea and substituted urea complexes of pentaamminecobalt(III). Only the O-bonded form was known for urea previously [14, 15] although both isomers were recently obtained for *N,N*-dimethylurea [16]. A general synthetic route to the N-bonded isomers for urea and for a variety of mono- and N,N-disubstituted derivatives is now available [17], while the O-bonded isomers are readily obtained [15] via the $[(NH_3)_5CoO_3SCF_3](CF_3SO_3)_2$ complex.

The urea complexes attract interest for several reasons. First, the N-bonded forms, isolated as their deprotonated $(NH_3)_5Co(NHCONRR')^{2+}$ complexes ($pK'_a \sim 3$), protonate in acid solution and rapidly isomerize to the O-bonded isomer (*vide infra*). Concurrent work on analogous carboxamide complexes reveals a similar process [17], although remarkably $(NH_3)_5Co(amide\text{-}N)^{3+}$ isomerize much more slowly. For both the amide and urea systems, hydrolysis (to yield $(NH_3)_5CoOH_2^{3+}$ plus free ligand) accompanies the linkage isomerization process, and we were interested in both the electronic and steric effects of the carbonyl substituent (alkyl *versus* amino) on both the rate and course of reaction. Another facet of these reactions is the site of protonation, at the bound nitrogen or remote oxygen center, and studies are described herein which establish this site, and the mechanistic implications are discussed. Secondly, there is an interest [14b, 16] in the chemistry of the Ni^{2+} containing enzyme urease [18] which rapidly degrades urea to NH_3, CO_2 and H_2O. Although O-coordination of urea to Ni^{2+} at the active site of the enzyme is favoured, there was a need to investigate model systems in which urea was both N- and O-bonded. Work on the O-bonded $(NH_3)_5CoOC(NH_2)_2^{3+}$ ion [14b] and other urea-*O* metal ion model systems (Co(III) [16], Rh(III) [19a], Cr(III) [19b], Ru(III) [19c]) has been described, and herein we report the behaviour of several $(NH_3)_5Co(urea\text{-}N)^{n+}$ systems which bear on this issue.

Finally, we report the specific rates and conditions for the observation of hitherto unrecognized urea-*O* to urea-*N* isomerization reactions. These results provide further comment on the mechanism of linkage isomerization [1], and permit the determination of thermodynamic data for the urea-*N*/urea-*O* equilibria and a comparison with a Rh(III) system [19].

Results and Discussion

Synthesis

The deep pink O-bonded urea complexes were prepared quantitatively by the reaction between the labile triflato complex $[(NH_3)_5CoO_3SCF_3](CF_3SO_3)_2$ and excess ligand in acetone solution, or in other non-coordinating solvents such as sulfolane [15, 16]. Crystallization from water as the sparingly soluble dithionate salts ensured the absence of the more water-soluble $[(NH_3)_5CoOH_2]_2(S_2O_6)_3$ complex. The more soluble perchlorate salts were obtained by treating the dithionate salts with cold 5 M $HClO_4$.

The N-bonded urea complexes were prepared by two routes. For NH_2CONRR', the synthesis [16] utilizing the facile base-catalyzed hydrolysis of the substituted cyanamide derivative $(NH_3)_5CoNCNRR'^{3+}$ is preferred since it is rapid and quantitative. The precursor cyanamide complexes are obtained easily [15] from the triflato compound. For the monosubstituted and unsubstituted urea ligands, this reaction fails because the precursor cyanamide complex exists as its stable deprotonated form $(NH_3)_5CoNCNR^{2+}$ in basic solution [16, 20]. However, using an alternative synthetic route, we have found that the urea ligands can be forced to bind through nitrogen [17]. Thus $(NH_3)_5CoOSMe_2^{3+}$ and excess urea in Me_2SO solvent containing the non-nucleophilic (and non-coordinating) bases 2,6-lutidine, 2,2',6,6'-tetramethylpiperidine or even triethylamine, readily yielded under controlled conditions the deprotonated

urea-*N* complexes in good yield. Base is required to shift the urea-*O*/urea-*N* equilibrium to favour the N-bonded form. The N-bonded anionic urea ligand is strongly preferred thermodynamically (H_2O, pK'_a urea-N^{3+}, ~3; pK'_a urea-O^{3+}, ~13) [16]. Attempts to effect a similar shift in equilibrium in non-coordinating solvents such as acetone or sulfolane were surprisingly fruitless – such solutions proved so moisture sensitive that the kinetically inert $(NH_3)_5CoOH^{2+}$ was formed preferentially.

We have so far been unable to obtain the N-isomers $(NH_3)_5CoNRCONRR'^{2+}$ derived from the N,N'-substituted ureas RNHCONHR' by the otherwise successful procedure described above; presumably these ions, alkylated at the donor nitrogen atom, are thermodynamically unstable with respect to their O-bonded forms, or side-reaction (hydrolysis or decomposition) is faster than the desired substitution process. Consistent with this view, the monosubstituted ureas methylurea and phenylurea yielded exclusively the N-bonded linkage isomers $(NH_3)_5CoNHCONHR^{2+}$ rather than $(NH_3)_5CoNRCONH_2^{2+}$ by the new synthetic route [17]. The urea-*N* complexes were crystallized as the red–pink perchlorate salts of the deprotonated cation, *i.e.* $[(NH_3)_5CoNHCONRR'](ClO_4)_2 \cdot xH_2O$ ($x = 1, 2$; R,R' = H, CH_3). Other salts such as those of $CF_3SO_3^-$ and NO_3^- were readily crystallized but not characterized. The unsubstituted urea-*N* complex formed a stoichiometric triflate/perchlorate salt, less soluble than either the di-triflate or di-perchlorate. Details of the general synthetic route to complexes containing N-bonded isomers of other ambidentate ligands such as amides $RCONH_2$, urethanes $ROCONH_2$, sulfonamides RSO_2NH_2, sulfamide $NH_2SO_2NH_2$, methanesulfinamide CH_3SONH_2 and sulfamate $H_2NSO_3^-$ are described elsewhere [17].

The protonated forms of the urea-*N* complexes could be crystallized as yellow plates or needles by treatment with the appropriate acid. The solids so obtained were shown by ^1H NMR spectroscopy and ion-exchange chromatography to have the stoichiometry $[(NH_3)_5Co(urea)]X_3$ and to consist largely if not entirely of the protonated N-bonded isomer. However, these solids rapidly isomerized to give the respective O-bonded urea complexes, even in the solid state ($t_{1/2}$ ~ min, 25 °C!). Therefore it proved generally more convenient to quantitatively and rapidly generate and observe the protonated N-isomers *in situ* in the appropriate solvent, H_2O, Me_2SO or Me_2CO.

Characterization

Aside from elemental analysis, the identity and purity of the urea complexes were established by ion-exchange chromatography on SP Sephadex C-25 or Dowex 50Wx2 cation exchange resins. The O-bonded isomers separate cleanly from the main impurity $(NH_3)_5CoOH_2^{3+}$, and other trace $(NH_3)_5CoX^{n+}$ impurities, using a sodium phosphate/sodium chloride (1:9) buffer (pH = 7) as the eluent. All urea-*O* samples used in this work were shown to be pure by this method. Also the ^1H NMR spectra in concentrated, dry DMSO-d_6 solution [21] readily established the absence of $(NH_3)_5CoOH_2^{3+}$. Similarly, the urea-*N* isomers were shown to be free of $(NH_3)_5CoOH^{2+}$ and other pentaammine complex impurities. Indeed, the usual synthetic procedure [17] entails a purification step involving ion-exchange chromatography in which the N-isomer is cleanly eluted as its deprotonated form $(NH_3)_5CoNHCONRR'^{2+}$ well separated from any O-bonded isomer $(NH_3)_5CoOC(NH_2)NRR'^{3+}$, starting material $(NH_3)_5CoOSMe_2^{3+}$, hydrolysis product $(NH_3)_5CoOH^{2+}$, and traces of $Co(NH_3)_6^{3+}$ which arise through a disproportionation reaction in preparations under forcing conditions.

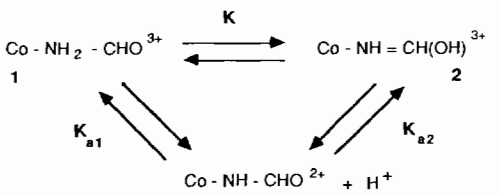
Isomeric purity was established by ion-exchange chromatography and ^1H and ^{13}C NMR spectroscopy, where all forms of the complex are distinguished from each other as well as from free ligand. The N- and O-bonded isomers readily separate chromatographically, as 2+ and 3+ ions respectively, using eluents having a pH above the pK'_a of the urea-*N* species. Phosphate based eluents (pH ~ 7) at low temperature (~5 °C) were employed, since the rate of spontaneous aquation at 25 °C ($t_{1/2}$ ~ 4 h) is not insignificant, while base-catalyzed hydrolysis of the urea-*O* isomers becomes increasingly important at higher pH. Also, the low pH region (≤3) was avoided because the N-bonded isomers isomerize rapidly to their O-bonded forms by an acid-catalyzed pathway (*vide infra*).

Isomer Assignments and Solution Structure

The distinction between N- and O-bonded urea isomers is made in several ways. The preparative chemistry and direct measurements establish the large difference in the pK'_a values for the urea protons; pK'_a ~ 3 for the urea-*N* and ~13 for the urea-*O* species. As pointed out previously [22, 23], metal ion coordination enhances the acidity of ligand protons, especially when these protons reside on the donor atom (although see below). For example, free urea has a pK'_a ~ 13.8, which is reduced slightly to ~13 on O-coordination [14] but substantially, to ~3, on N-coordination. This ~10^{10}-fold dimunition in pK'_a for the N-bonded isomer is similar to that found for sulfamate ion $NH_2SO_3^-$ [23], formamide NH_2CHO [24] and cyanamide $NCNH_2$ [20], all N-bound to Co(III).

Because species such as $(NH_3)_5CoOH_2^{3+}$ and the N-bonded isomers above are substantially more acidic than the free ligands (~10^8–10^{12}-fold), compared to ions such as $(NH_3)_5CoO_3P(OH)^+$ where H^+ resides on the *exo*-oxygen and the enhancement is only ~10^2, it has been assumed in ambivalent cases [22–24] that the proton must reside on the donor atom. However

this reasoning is incorrect, and the point is illustrated for the N-bonded formamide complex $(NH_3)_5Co(NH_2CHO)^{3+}$. For the following system of cyclic equilibria



it can be seen readily that $K = K_{a1}/K_{a2}$, and if $K_{a1} \gg K_{a2}$ then obviously K is large. Thus the protonated formamide-*N* complex should exist in the iminol form **2** where the proton resides on the *exo*-electronegative atom! In fact, recent ^1H NMR work [17] establishes the N-bonded isomer to be $(NH_3)_5CoNH{=}CH(OH)^{3+}$ rather than $(NH_3)_5CoNH_2CHO^{3+}$ as originally believed [24]. This actually supports a case for enhanced acidity of protons adjacent to the metal ion, since when the proton does not reside on the donor atom, as here, the enhancement must be even greater than the observed factor.

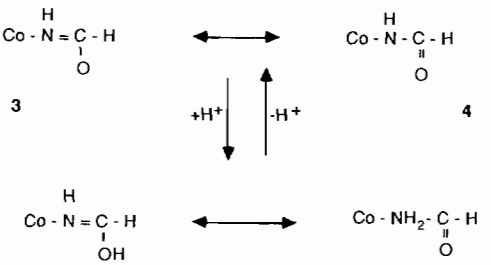
We believe that the N-bonded complexes of amides, ureas and other N,O-bonded ambidentate ligands are appreciably more acidic than the corresponding O-bonded forms because the conjugate base is significantly more resonance stabilized. Such stabilization is available to either the amide **1** or iminol form **2** of the N-isomers. Indeed, the NMR data discussed ahead show that the urea-*N* species have the structure $Co{-}NH_2COR^{3+}$, rather than $Co{-}NH{:}C(OH)R^{3+}$ like the amide-*N* species even though they are of comparable acidity (pK'_a 2–3). In summary, acidity arguments, while not definitive of the site of protonation for the N-isomers, still provide a useful empirical distinction between urea-*N* and urea-*O* bonding.

The pK'_a values for the O-bonded urea and *N,N*-dimethylurea species indicate a negligible effect attributable to N-methylation; the urea-*O* species is close to twice as acidic (pK'_a 13.2 *versus* 13.5), as the statistical expectation [16]. In this article it will be generally assumed that *exo*-NH_2 alkylation has little effect on the pK'_a of the N-bonded urea species; the pK'_a has been measured accurately only for the $(NH_3)_5CoNH_2CON(CH_3)_2^{3+}$ ion (2.9, 25 °C; μ = 1.0 M, KCl) [16].

The relative acidities of the N- and O-bonded urea complexes are important for another reason. They control the thermodynamics of the urea complexation process as noted earlier, and thus, depending upon the pH, they determine whether O- to N- or N- to O-bonded urea rearrangement can actually be observed.

The electronic absorption spectra (see Table VIII) also reflect the mode of urea coordination. The O-bonded isomers are pink, ϵ_{520}(max) ~ 85, indicating a ligand field strength similar to, for example, the pink O-bonded $OP(OCH_3)_3$ (ϵ_{518}(max) 49.3), OSO_3^{2-} (ϵ_{516}(max) 63.9) and OCO_2^{2-} (ϵ_{510}(max) 92.0) complexes. The spectra of the deprotonated N-bonded isomers (ϵ_{500}(max) ~ 100) do not provide a direct comparison since the urea is bonded as its anion. However, the comparable protonated urea-*N* species absorb at significantly higher energies (ϵ_{485}(max) ~ 70) than the O-bonded species, consistent with the increased ligand field expected for N-coordination (*cf.* $(NH_3)_6Co^{3+}$, ϵ_{475}(max) 57.6, $(NH_3)_5CoNO_2^{2+}$, ϵ_{457}(max) 96.0, $(NH_3)_5CoONO^{2+}$, ϵ_{491}(max) 70.5).

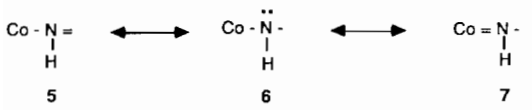
From the visible absorption spectra, the protonated N-bonded sulfamate, amide and sulfonamide complexes have been argued to be uniformly of the form $(NH_3)_5Co{-}NH_2{-}R^{3+}$, *i.e.* protonated at nitrogen [22–24]. However there is no precedent to suggest that the O-protonated N-isomers $(NH_3)_5Co{-}NH{=}C(OH)R^{3+}$ might differ significantly in ligand field absorption, and it is revealing to observe that the lower energy ligand field band for the protonated N-isomers of sulfamate, sulfamide, sulfonamides and ureas all occur in a remarkably narrow range, at ~488 nm (ϵ ~ 60). The corresponding absorption for the protonated N-amides occurs at ~478 nm (ϵ ~ 70). This consistent difference, albeit small (~10 nm), suggests a different site of protonation for the amides. Furthermore, for all the deprotonated N-ligand species, N-amides excepted, large changes in the visible absorption spectra occur on protonation. This can be understood if the N-amide, $(NH_3)_5CoNHCHO^{2+}$ being typical, has a greater imine character **3** than the other N-bonded species,



Thus O-protonation of **3**, in contrast to N-protonation, does little to disrupt the chromophore, accommodating the relatively small change in the electronic spectrum. The proton on the *exo*-oxygen 'locks' the ligand in the iminol form, and the visible absorption spectral data indicates that this group ($Co{-}NH{=}C(OH)R$ λ(max) ~ 476 nm) exerts a stronger ligand field than in $Co{-}NH_2{-}R$ (λ(max) ~ 488 nm; R = $-CONR'R''$, $-SO_3^-$, $-SO_2NH_2$, $-SO_2NR'R''$, $-S(O)R'$), but coincidentally it is very similar to that of NH_3 (λ(max) = 465 nm). The amine ligands of the latter $Co{-}NH_2R$ complexes, because of the electron-withdrawing R substituents, are weaker bases than

NH_3, and accordingly there is a 12 nm shift to lower energies.

The above provides a rational basis for the interpretation of the visible absorption spectra of the deprotonated N-isomers. The series of complexes $A_5CoNHCOR^{2+}$ (ϵ(max) = 80), $A_5CoNHSO_2R^{2+}$ (ϵ(max) = 90), $CoNHCONR_2^{2+}$ (ϵ(max) 90–110) and $CoNHSO_3^+$ (ϵ(max) = 117) show a systematic decrease in energy concomitant with an increase in intensity for the first ligand field band. This is consistent with a gradual shift from the imine **5** to an aminate donor **6**.



5 **6** **7**

For the aminate extreme, the lone pair of electrons on nitrogen can contribute to ligand-to-metal π-bonding, **7**, an effect known to reduce the ligand field and increase the intensity of the d–d transition. The large change in absorption spectra on protonation – the shift to higher energy and reduction in intensity – is therefore consistent with proton addition to the donor N-center for all the N-bonded species above except the amides.

In summary, the O- and N-bonded urea complexes are clearly differentiated in the electronic spectra. For the protonated N-bonded ligands, there is a consistency in the data for a variety of N-bonded ligands, indicative of the $CoNH_2$–CO–R^{3+} tautomer (rather than CoNH=C(OH)R^{3+}). The spectra of the protonated amides are different, and consistent with the alternative tautomer. For the deprotonated N-bonded complexes, the visible spectra indicate the degree of electron-delocalization into the CoN–C bond, greatest for the amides (Co–NH=C) and weaker for sulfamide, sulfonamides, ureas and sulfamate ion (Co–NH–C).

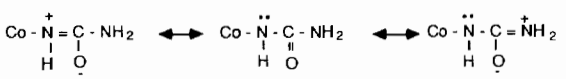
It has been recorded previously that the ^{1}H NMR spectra are diagnostic of the mode of coordination of N/O ambidentate ligands [22]. The bonding mode criterion is based on the difference in chemical shift between the *cis*- and *trans*-NH_3 protons of $(NH_3)_5CoX^{n+}$, characteristic of the nature of X. For all the urea complexes assigned as O-bonded, this difference is substantial, 1.2–1.4 ppm, while for the deprotonated N-bonded urea complexes the difference is small, 0–0.2 ppm (Table I). We note that this small chemical shift difference is exhibited also by the protonated N-bonded isomers (Table I), and hence the ^{1}H NMR method of isomer assignment is not contingent upon whether urea is coordinated as a neutral ligand or as its anion. The absolute chemical shifts are somewhat solvent dependent but the chemical shift differences are not.

The absolute chemical shift of the *cis*-NH_3 signal (12H) is also diagnostic of the mode of coordination. For the urea-*O* complexes in DMSO-d_6, this occurs 3.8–4.0 ppm downfield from TMS, while for the deprotonated urea-*N* species this signal appears at a consistently higher field, 3.2–3.3 ppm. This difference between the isomers, ~0.7 ppm, is substantial in comparison to the almost negligible effect of the number and nature of the N-substituents on the urea ligand.

The ^{1}H NMR spectra of a wide range of $(NH_3)_5CoX^{n+}$ complexes (X = urea, amide, sulfamide, sulfinamide, sulfonamide, and others) have been examined [17] with a view to independently ascertaining the site of protonation in N-coordinated species, and in particular for the urea complexes $(NH_3)_5CoNHCONRR'^{2+}$. However, neither the absolute chemical shifts of the Co–NH_3 signals nor the chemical shift differences between the *cis*- and *trans*-NH_3 signals can be easily related to the site of protonation. For example the species $(NH_3)_5CoNH$=CH(OH)$^{3+}$ and $(NH_3)_5CoNH_2$–SO_3^{2+}, protonated at oxygen and nitrogen respectively, show very similar *cis*- and *trans*-NH_3 signals. Indeed, this example serves to emphasize the value of the ^{1}H NMR technique in assigning the nature of the donor atom, *i.e.* distinguishing linkage isomers, since the Co–NH_3 chemical shifts appear to be insensitive to the subtleties of ligand tautomerism.

The deprotonated N-isomers are of course distinguished from the O-bonded forms and free urea ligands by the reduced NH proton count in the ^{1}H NMR spectra (Me_2SO-d_6). The $(NH_3)_5CoNHCONH_2^{2+}$ ion, for example, shows the *exo*-NH_2 protons as a singlet at δ 5.00 (2H) and the coordinated iminate NH(1H) at δ 1.62 (integration relative to the 15 Co–NH_3 protons). The ligand absorptions also serve to distinguish $(NH_3)_5CoNHCON(CH_3)H^{2+}$ from its linkage isomer $(NH_3)_5CoN(CH_3)CONH_2^{2+}$. The deprotonated *N*-methylurea complex shows a high field NH singlet characteristic of Co–NH– (δ 1.50, 1H), and the *exo*-NH as a lower field quartet (δ 5.38, 1H, J = 4.5 Hz). The same CH_3–NH coupling is observed for the methyl resonance (Table I). A similar argument can be advanced to support the $(NH_3)_5CoNHCONH(C_6H_5)^{2+}$ isomer assignment (Table I).

An unusually high field Co–NH– signal is observed for all the deprotonated urea-*N* species, as well as for a variety of other $(NH_3)_5CoNHR^{2+}$ ions, R = $-SO_3^-$, $-SO_2NH_2$, $-SO_2R$, $-CO(OR)$ (Table I). This can be interpreted as indicative of an appreciable contribution to the resonance hybrid from the aminate structures **9**, **10**.



8 **9** **10**

TABLE I. Proton NMR Chemical Shift Data for Ureas and their N- and O-bonded Complexes $(NH_3)_5Co(urea)^{n+}$

Ligand	Free ligands, δ (ppm)[a]			
	NH_2	NH	CH_3	Other[d]
NH_2CONH_2	5.62			
$NH_2CONHCH_3$	5.42	5.77, q (*J* 4.5)	2.52, d (*J* 4.5)	
$NHCH_3CONHCH_3$		5.77, q (*J* 4.5)	2.58, d (*J* 4.5)	
$NH_2CONHC_6H_5$	5.80	8.45		7.17; 7.30
$NH_2CON(CH_3)_2$	5.73		2.80	

	Complexes δ (ppm)[a]				
	cis-NH_3	*trans*-NH_3	CoNH	CONH	Other[d]
$CoNHCONH_2^{2+}$	3.22	3.07	1.62	5.00	
$CoNHCONHCH_3^{2+}$	3.22	3.07	1.50	5.38, q (*J* 4.5)	2.53, d (*J* 4.5)
$CoNHCONHC_6H_5^{2+}$	3.38	3.20	2.02	8.25	7.15; 7.28[d]
$CoNHCON(CH_3)_2^{2+}$ [b]	3.23	3.05	1.80		2.80
$CoNH_2CONH_2^{3+}$	3.60	3.30	5.95	7.15; 7.65	
$CoNH_2CONHCH_3^{3+}$	3.70	3.40	6.27	7.87, q (*J* 4.5)	2.70, d (*J* 4.5)
$CoNH_2CONHC_6H_5^{3+}$	3.65	3.37	[e]	9.32	7.37; 7.47[d]
$CoNH_2CON(CH_3)_2^{3+}$ [b]	3.66	3.36	[e]		2.94
$CoOC(NH_2)_2^{3+}$ [c]	3.90	2.50		6.62	
$CoOC(NH_2)NHCH_3^{3+}$	3.93	2.60		6.53[f]; 6.77, q (*J* 4.5)	2.60, d (*J* 4.5)
$CoOC(NHCH_3)_2^{3+}$	3.85	2.62		6.43, q (*J* 4.5)	2.63, d (*J* 4.5)
$CoOC(NH_2)NHC_6H_5^{3+}$	4.02	2.70		6.67[f]; 8.95	7.15; 7.22
$CoOC(NH_2)N(CH_3)_2^{3+}$	3.95	2.68		6.33	2.75

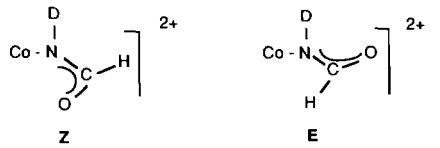
[a]ppm downfield from TMS in Me_2SO-d_6 at 35 °C. [b]Data from ref. 16. [c]Data from ref. 14b. [d]Methyl or phenyl resonances; shifts recorded only for the two most prominent phenyl spikes. [e]Not observed; average $CoNH_2/H^+/H_2O$ signal at 35 °C. [f]$OC(NH_2)$.

This NH signal may be contrasted with that observed for the deprotonated amides at lower field (δ ~ 4–5 ppm), consistent with increased π-electron-delocalization into the CoN–C amide bond, *i.e.* increased imine character (Co–NH=, 8). This rationale is consistent with that deduced from the visible absorption spectra.

Two predictions follow from these conclusions. First, in the imine form 8 the oxygen should be the basic center while it is likely to be nitrogen for the iminate form **9**. Resonance between forms **9** and **10** for the ureas should reduce the contribution from 8, and hence the basicity of oxygen relative to nitrogen. While this simple explanation satisfactorily accounts for the propensity of the amides to O-protonate and the ureas to N-protonate, it need be recalled that the pK'_a values for the urea-*N* and amide-*N* complexes are similar (2–3). Thus, the overall basicity of the deprotonated N-complexes seems to be essentially constant, *i.e.* the basicity of alternative centers is mutually dependent.

The second prediction is that the CoN–C bond order in the deprotonated species should be greater for the amides than the ureas. This is not clear from available C–N bond length data for an amide $(NH_3)_5CoNHCOCH_3^{2+}$ and a urea $(NH_3)_5CoNHCON(C_6H_5)H^{2+}$ complex (131.1(1.4) and 133.9(1.2) pm, respectively [26, 27]. However another consequence of an increased C–N bond order is the phenomenon of restricted rotation about the partial double bond. Free amides R_2NCOR', *N,N*-dimethylformamide being the classic example, show separate resonances for the inherently diastereotopic R groups in the ambient temperature NMR (^1H, ^{13}C) spectra, and

these may be coalesced at higher temperatures. In contrast free ureas $R_2NCONRR'$ rarely exhibit this behaviour, presumably because of lower C–N bond orders. This situation possibly extends to their deprotonated N-bonded pentaamminecobalt(III) complexes, although the data are presently limited. Balahura and Jordan [24] claimed to have frozen out in the low temperature ^1H NMR spectra the *Z* and *E* isomers arising from restricted rotation in the N-coordinated amide $(NH_3)_5CoNDCHO$.



We have been unable to achieve this for at least two of the corresponding urea-*N* complexes, $(NH_3)_5CoNHCONH_2^{2+}$ and $(NH_3)_5CoNHCON(CH_3)_2^{2+}$, for both the ^1H and ^{13}C NMR spectra of Me_2CO-d_6 or DMF-d_7 solutions down to −30 °C (Tables I and II). While these observations are consistent with the argument, it is recognized that the intrinsic chemical shift differences between the *exo*-R groups (which are unknown) affect the coalescence temperatures.

TABLE II. Carbon-13 NMR Chemical Shift Data for Ureas and their N- and O-bonded Complexes $(NH_3)_5Co(urea)^{n+}$

Ligand	Free ligands, δ (ppm)[a]		
	CO	NCH_3	Other[c]
NH_2CONH_2	160.69		
$NH_2CONHCH_3$	159.47	26.17	
$NHCH_3CONHCH_3$	159.52	26.17	
$NH_2CONHC_6H_5$	156.05		140.37; 128.45 (2C); 121.03; 117.75 (2C)
$NH_2CON(CH_3)_2$	159.03	35.81	
	Complexes, δ (ppm)[a, b]		
$CoNHCONH_2^{2+}$	168.00		
$CoNHCONHCH_3^{2+}$	167.40	27.66	
$CoNHCONHC_6H_5^{2+}$	163.48		141.54; 128.29 (2C); 119.87; 117.73 (2C)
$CoNHCON(CH_3)_2^{2+}$	166.46	36.52	
$CoOC(NH_2)_2^{3+}$	165.69		
$CoOC(NH_2)NHCH_3^{3+}$	161.46	30.53	
$CoOC(NHCH_3)_2^{3+}$	162.74	27.47	
$CoOC(NH_2)$-$NHC_6H_5^{3+}$	161.66		137.09; 129.08 (2C); 123.36; 121.36 (2C)
$CoOC(NH_2)$-$N(CH_3)_2^{3+}$	162.20	36.76	

[a]ppm downfield from TMS in Me_2SO-d_6 at 30 °C; dioxane reference (66.26 ppm); [free ureas] ~ 0.1 M. [b][Complex] ~ 0.2 g/1.5 ml; ClO_4^- salts. [c]The phenyl carbons are ordered thus: α to N(1C), *ortho* (2C), *para* (1C), *meta* (2C).

However, definitive evidence for restricted rotation can be found for the ligand absorptions in the ^1H NMR spectra of the protonated urea-*N* complexes, as discussed below. As well, the NMR data are diagnostic of protonation at nitrogen for these two urea-*N* complexes.

The ^1H NMR spectra of $(NH_3)_5CoNHCONH_2^{2+}$ in Me_2SO-d_6, and in Me_2SO-d_6 containing a slight molar excess of CF_3COOH, are shown in Fig. 1 for the NH region; the temperature dependence (inset) is only qualitative. A 1:1:2 pattern (5–8 ppm, a:b:c) is apparent for the intensity of the NH signals for the protonated form, confirmed by integration. Furthermore it is clear that the two lower field signals are in coalescence identifying these as the diastereotopic *exo*-NH_2 protons arising from restricted rotation about this C–N bond. The two-proton signal at

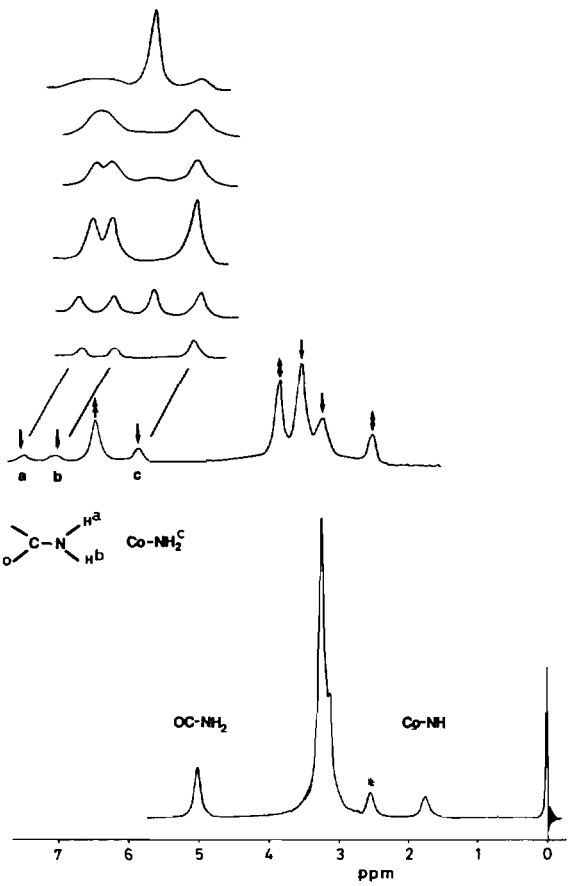
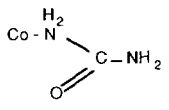


Fig. 1. ^1H NMR spectra of $(NH_3)_5Co(urea)^{n+}$ in Me_2SO-d_6 at 35 °C. Bottom spectrum: $(NH_3)_5CoNHCONH_2^{2+}$ (* = residual Me_2SO-d_5). Top spectrum: $(NH_3)_5CoNH_2CONH_2^{3+}$ generated *in situ* by addition of CF_3CO_2H, and undergoing isomerization to $(NH_3)_5CoOC(NH_2)_2^{3+}$; the arrows indicate the direction of change with time. Inset to top spectrum: the urea ligand region, at various temperatures (and stages of N- to O-isomerization), showing that the *exo*-NH_2 protons are inequivalent and can undergo coalescence (~40 °C).

higher field (c) can then be assigned to Co–NH_2–. This is separate from a lower field resonance (>10 ppm) of variable intensity and chemical shift, depending upon the relative quality of added acid, which is clearly attributable to CF_3COOH/H^+. These observations strongly indicate structure **11** for the protonated form, and seem to exclude the alternative O-protonated iminol forms **12** and **13**. *A priori*, **13** could accommodate the NMR chemical shifts (but not the coalescence phenomenon), but it is our experience that –OH protons of this kind are in rapid exchange with free acid on the NMR time scale, contrary to the observation. Moreover, N-protonation shown in **11** removes the π-electron delocalization from the $CoNH_2$–C bond rendering amide character to the ligand; this nicely accommodates the (increased) restricted rotation about the $CoNH_2C(O)$–N bond, characteristic of amides.



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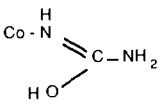

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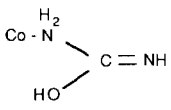

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The *N*-methylurea-*N* complex, like the parent urea-*N* species, could be strongly argued to protonate on nitrogen. The *exo*-NH appears as a quartet (J = 4.5 Hz) at δ 7.87, downfield 2.5 ppm from the corresponding signal in the deprotonated form, and fully consistent with a structure like **11**. The $CoNH_2$– signal is observed at δ 6.27, close to that observed for the unsubstituted urea complex (δ 5.95). The *Z* and *E* isomers arising from restricted rotation about the $CoNH_2C(O)$–N bond are not observed; very likely one isomer is preferred, although the NMR data do not allow an unambiguous decision as to which. That having the Me group *trans* to the carbonyl is more consistent with the data, since the NH signal at δ 7.87, correcting for the effect of methyl substitution, corresponds quite closely to the lower field NH of the unsubstituted urea analog at δ 7.65, presumed *cis* to CO.

The dimethyl- and phenylurea-*N* complexes are unusual in that the $CoNH_2$– and free acid signals are exchange-averaged, precluding a definitive assignment of the site of protonation. Nonetheless the *exo*-NH signal for the phenylurea complex shows a large downfield shift (1.88 ppm) on protonation, although not as large as that observed for the methylurea (~2.5 ppm) and urea (~2.5 ppm) species. This result suggests a common tautomeric form, while an independent case for N-protonation of the dimethylurea species was mounted previously [16].

The O-bonded urea complexes, for which all ligand NH protons are exo, show absorptions intermediate between the Co–NH_2– (higher field) and *exo*-NH (lower field) signals for the protonated N-isomers. Diastereotopic groups or *Z*/*E* isomers arising from restricted rotation about the C–N bond(s) are not found in the ambient temperature ^1H or ^{13}C NMR spectra, although Co(III) coordination was anticipated to raise the rotational barrier. Also, the data do not permit a clear decision on the ligand isomer adopted by the *N*-methylurea-*O* and *N*-phenylurea-*O* species since at the moment we have not separated chemical shift data for the NH protons *cis* and *trans* to the carbonyl group in for example $(NH_3)_5CoOC(NH_2)_2^{3+}$ or $(NH_3)_5CoOC(NH_2)NHCH_3^{3+}$.

Spontaneous and Base-catalyzed Solvolysis of the Urea-O Complexes

The title complexes react slowly but completely in acidic H_2O and in Me_2SO.

$$(NH_3)_5CoOC(NHR)NRR'^{3+} \xrightarrow{sol} (NH_3)_5Co(sol)^{3+} + RNHCONRR'$$

^1H, ^{13}C NMR spectroscopy and ion-exchange chromatography established the stoichiometry. The specific rates k_s are insensitive to N-methyl substitution, but the N-phenyl derivative is appreciably more reactive (~5-fold, Table III). In Me_2SO solvolysis is slower or faster depending upon the substituents, but the variations are not large (~3-fold). The faster rates in Me_2SO may be attributed to solvent destructuring by the *N*-phenyl and *N*,*N*-dimethyl substituents.

The hydrolysis reactions are appreciably base-catalyzed. The urea-*O* and *N*,*N*-dimethylurea-*O* complexes follow a rate law of the form

$$k(\text{obs.}) = k_1 + k_2[OH^-]$$

where $k_1 \sim 3 \times 10^{-5}$ s^{-1} (Table III) and $k_2 \sim 10$ M^{-1} s^{-1} (μ = 1.0 M, 25 °C). Above pH ~ 11, a term inverse in $[OH^-]$ becomes significant, attributable to net deprotonation of the urea-*O* species to yield $(NH_3)_5$-

TABLE III. Solvolysis Rate Data for $(NH_3)_5Co(\text{urea-}O)^{3+}$ Complexes at 25 °C

Ligand	$10^5 \times k$(obs.) (s^{-1})			
	0.1 M $HClO_4$[a]	1.0 M $HClO_4$	0.1 M Na.MES[a, b]	Me_2SO
$OC(NH_2)_2$	3.95	4.0[c]	4.86	1.88
$OC(NH_2)NHCH_3$	2.95		3.24	1.53
$OC(NHCH_3)_2$	3.36		3.73	4.24
$OC(NH_2)N(CH_3)_2$	3.05		(3.8[d])	1.73
$OC(NH_2)NHC_6H_5$	16.1			48.2

[a] μ = 1.0 M ($NaClO_4$). [b] pH 6.3, 1/2-neutralized (NaOH). [c] Value from Table II, Supplementary Material, ref. 14b. [d] Value from ref. 16. [e] Mean of at least three determinations; standard deviations ± 3% generally.

$CoOC(NH)NRR'^{2+}$ ($pK'_a \sim 13$) [14b, 16]. Although the complete rate law does not require it, other evidence [16] suggests that the urea-*O* complexes, when deprotonated on the ligand, are relatively unreactive.

We have not measured k_{OH} for the methylurea, phenylurea or *N,N'*-dimethylurea complexes but have determined that $k_{OH} > 5$ M^{-1} s^{-1} since reaction in 0.1 M OH^- is complete inside 10 s. There is no reason to believe that the same rate law does not pertain for all the urea-*O* species.

Both Co–O (97.5%) and C–O (2.5%) cleavage paths have been exposed by ^{18}O-tracer experiments on the unsubstituted urea-*O* complex [14], and anion competition work has shown that there is a greater proportion of C–O cleavage in the presence of some anions, especially Y^{2-} (SO_4^{2-}, $S_2O_3^{2-}$). However, anion competition experiments for the dimethylurea-*O* complex indicate that Co–O cleavage is the exclusive reaction mode, even in the presence of Y^{2-}.

None of the previous nor presently studied urea-*O* species hydrolyze with detectable (≤0.5%) C–N cleavage. This is also true of the base-catalyzed reactions [14, 16, 17] considered ahead, as well as for reaction under acid-catalyzed conditions (3 M HCl). Certainly the carbamate-*O* species would survive the conditions of base hydrolysis ($k_{OH} \ll 1$ M^{-1} s^{-1}, 25 °C) and chromatography (at pH > 2; $t_{1/2} > 1$ h, 25 °C) [28]. Even the phenylurea-*O* complex yielded neither $(NH_3)_5CoO_2CNH_2^{2+}$ nor $(NH_3)_5CoO_2CNHC_6H_5^{2+}$ in OH^-, where the good leaving group aniline $C_6H_5NH_2$ offered the best prospect. While the $(NH_3)_5Co(III)$ moiety must activate the O-bound urea towards C–N cleavage, it is apparent that $k_{OH} < 0.1$ M^{-1} s^{-1} for this path since base-catalyzed Co–O cleavage ($k_{OH} \geq 5$ M^{-1} s^{-1}) still wins handsomely.

The contrast with amide-*O* complex chemistry [17, 29] is worth emphasizing, although a satisfactory account is lacking. The difference does not arise simply because the urea-*O* species react by Co–O cleavage more rapidly than the amides, thereby masking C–N cleavage. Indeed recent work [17] indicates that the amide-*O* species base-hydrolyze at comparable or greater rates, for both Co–O and C–N bond rupture. The same is true of C–N cleavage for the free urea and amide ligands.

Base-catalyzed O- to N-linkage Isomerization

This reaction was not detected in earlier work on the urea-*O* and dimethylurea-*O* systems. Although O- to N-rearrangement cannot be observed in acid solution (pH < 3) because the N-/O-bonded urea isomer equilibrium lies fully to the side of the O-bonded isomer, it is observable in principle above pH ~ 3 where the N-bonded isomer assumes thermodynamic stability as its deprotonated form $(NH_3)_5CoNHCONRR'^{2+}$.

The urea-*N* and urea-*O* complexes are relatively stable and can be separated by ion-exchange chromatography at pH 7 using phosphate based eluents. Phosphate ion buffer (pH 7) moves $(NH_3)_5CoOH_2^{3+}$ unusually rapidly, as if a 2+ ion, and by adjusting the Cl^-, $HPO_4^{2-}/H_2PO_4^-$ (1:1) ratio in the eluent a clear separation of all three complexes is obtained. By the same technique, the urea-*O* substrates were shown to be free of N-bonded isomer impurity. Thus the observation that when reacted in 0.1–1.0 M OH^- they produced significant and reproducible amounts of $(NH_3)_5CoNHCONRR'^{2+}$ (3–8%), along with $(NH_3)_5CoOH^{2+}$ (92–97%) is significant. Only the one urea-*N* product is found for the unsymmetrical *N*-methylurea and *N*-phenylurea species which in principle could also have yielded $(NH_3)_5CoNRCONH_2^{2+}$. Capture by the $N(CH_3)_2$ group in the case of the *N,N*-dimethylurea complex, to give $(NH_3)_5CoN(CH_3)_2CONH_2^{3+}$, cannot be observed since it lacks the necessary acidic Co–NHR– proton for stabilization by deprotonation.

The product distributions (Table IV) are slightly ionic strength dependent, but independent of $[OH^-]$ over at least a 10-fold range in the high pH region (>13) where reaction is entirely via the base-catalyzed path. It follows that the rate law for the urea-*O* to urea-*N* rearrangement is identical to that for base-catalyzed hydrolysis, even under conditions where appreciable net deprotonation of $(NH_3)_5CoOC(NH_2)NRR'^{3+}$ occurs (~50% at 1 M $[OH^-]$). The inference is that the same intermediate or equilibrated set of intermediates are involved.

In the earlier work [14, 16] concerned with urea complexes the interest vested in the observation of $(NH_3)_5CoO_2CNRR'^{2+}$ arising from C–N cleavage, but none was detected. For product analyses, product mixtures were acidified under which conditions any urea-*N* species would have rapidly isomerized back to their O-bonded isomers via their protonated forms. Although the aqua and urea-*O* complexes can be separated chromatographically, in both of the original studies the 3+ aqua ion was removed from the column as its more readily eluted 2+ hydroxo form at pH ~ 11; under these conditions the urea-*O* species base-hydrolyze readily, and therefore went undetected.

It is difficult to decide if the hydrolysis reaction as well as the O- to N-linkage isomerization reaction follow separate pathways from the common precursor aminato complex $(NH_3)_4(NH_2)CoOC(NH_2)NRR'^{2+}$. The dependence of the product distribution on the nature of the N-substituents (Table IV) can be explained by a common intermediate $(NH_3)_4(NH_2)CoOC(NH_2)NRR'^{2+}$ whereby H_2O and the amine group compete for the vacant coordination site. The product distribution is essentially independent of the urea substituents, save for a statistical factor of two which accommodates NH_2CONH_2 being twice as effective as NH_2CONRR'. Note that $-N(CH_3)_2$, $-NHCH_3$ and $-NHC_6H_5$ do not compete

TABLE IV. Product Distribution Data for the Reactions of $(NH_3)_5Co(urea\text{-}O)^{3+}$ Complexes at 25 °C

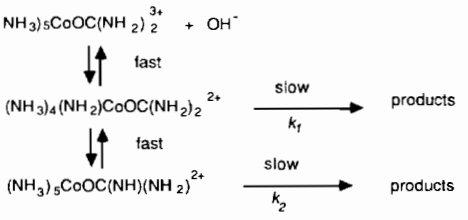
Ligand	Reagents	$Co(urea\text{-}N)^{2+}$ (%)	$CoOH^{2+}$ or $CoOH_2^{3+}$ (%)
$OC(NH_2)_2$	0.1 M NaOH [a]	7.9	92.1
	1.0 M NaOH [b]	7.2	92.8
	0.1 M NaOH [b]	7.1	92.9
	0.1 M NaOH [c]	6.3	93.7
	0.1 M Na.MES [b]	24.7[d]	75.3[d]
		20[e]	80[e]
	0.1 - 1.0 M $HClO_4$ [b]	0	100
$OC(NH_2)N(CH_3)_2$	0.1 M NaOH [b]	3.5	96.5
	0.1 M Na.MES [b]	17[f]	83[f]
		16.4[g]	83.6[g]
	0.1 - 1.0 M $HClO_4$ [b]	0	100
$OC(NH_2)NHCH_3$	0.1 M NaOH [b]	3.8	96.2
	0.1 M Na.MES [b]	9.9	90.1
	0.1 - 1.0 M $HClO_4$ [b]	0	100
$OC(NHCH_3)_2$	0.1 M NaOH [b]	0	100
	0.1 M Na.MES [b]	0	100
	0.1 - 1.0 M $HClO_4$ [b]	0	100
$OC(NH_2)NHC_6H_5$	0.1 M NaOH	3.2	97.0
	0.1 M Na.MES	8.2	91.8
	0.1 M $Na.H_nPO_4$ (pH 6.88)	8.9	91.0

[a] μ = 3.0 M ($NaClO_4$). [b] μ = 1.0 M ($NaClO_4$). [c] μ = 0.1 M ($NaClO_4$). [d] Approx. 81% reaction; results (±0.4%) normalized to 100% reaction. Actual recoveries: N-isomer, 20%; $CoOH_2^{3+}$, 61%; O-isomer, 19%. [e] Approx. 36% reaction; results (±1.5%) normalized to 100% reaction. Actual recoveries: N-isomer, 7%; $CoOH_2^{3+}$, 29%; O-isomer, 64%. [f] Approx. 33% reaction (~3.5 h); results (±1.5%) normalized to 100% reaction. Actual recoveries: N-isomer, 5.4%; $CoOH_2^{3+}$, 27.1%; O-isomer, 67.5%. [g] Approx. 85% reaction (~21 h); results (±0.4%) normalized to 100% reaction. Actual recoveries: N-isomer, 13.9%; $CoOH_2^{3+}$, 71.0%; O-isomer, 15.0%.

with $-NH_2$ and H_2O for coordination. For such *N,N'*-alkyl- or aryl-ureas, we have been unable to force O- to N-linkage isomerization to yield $(NH_3)_5CoNRCONR'R''^{2+}$, even under basic conditions in non-coordinating solvents. Thus it seems that this reaction is not favoured thermodynamically, and thus it is not observable.

Other work has demonstrated that amine nitrogens are exceedingly poor competitors in the base-hydrolysis reaction. For example there is no detectable $(NH_3)_6Co^{3+}$ (<0.2%) when $(NH_3)_5CoX^{n+}$ is base-hydrolyzed in 1 M NH_3 [30]. Also, negligible (<0.2%) capture of urea is found for the base hydrolysis of $(NH_3)_5CoO_3SCF_3^{2+}$ in 1.0 M NH_2CONH_2 at pH 9, and even the pendant-NH_2 group of ethylenediamine is not captured [31] in the base hydrolysis of $(en)_2CoCl(NH_2CH_2CH_2NH_2)^{2+}$. These observations suggest that the urea-*N* species observed in the base-hydrolysis of $(NH_3)_5CoOC(NH_2)NRR'^{3+}$ do not arise via competition between urea and water for the five-coordinate $(NH_3)_4(NH_2)Co^{2+}$ intermediate. Rather, the results strongly imply that the urea moiety, once dissociated from Co(III), is not recaptured and that hydrolysis ensues. We infer that O- to N-linkage isomerization is a concerted intramolecular process, separate from the accompanying (and dominant) hydrolysis process. For this reason k_{OH}(obs.) values have been segmented into k_{ON} and k_{OH} for the individual pathways (Table V), using the product distributions (Table IV).

In view of the fact that the urea-*O* complexes deprotonate in strong OH^-



it is tempting to ascribe hydrolysis to the aminato complex and linkage isomerization to the $(NH_3)_5CoOC(NH)(NH_2)^{2+}$ tautomer, because linkage isomerization usually involves anionic nucleophiles (e.g., NO_2^-, SCN^-, $S_2O_3^{2-}$, $NH_2SO_3^-$). However, it was noted previously [16] that the tautomeric equilibrium is pH independent and its position is governed by the relative pK'_a values, >15 and ~13 respectively. Furthermore the first-order rate constant k_2 must be of the order 1 s^{-1} to accommodate the

TABLE V. Specific Rates for the Spontaneous and Base-catalyzed Linkage Isomerization/Hydrolysis Reactions of $(NH_3)_5Co$-(urea-*O*)$^{3+}$; μ = 1.0 M, 25 °C

Ligand	Spontaneous path k (s^{-1})			Base-catalyzed path k (M^{-1} s^{-1})		
	$10^6 \times k_s$	$10^6 \times k_{ON}$	N-isomer[a, b] (%)	k_{OH}	k'_{ON}	N-isomer (%)
$OC(NH_2)_2$	39.5	12.8	24.5	14.2	1.1	7.2
$OC(NH_2)N(CH_3)_2$	30.5	6.0	16.4	9.9	0.36	3.5
$OC(NH_2)NHCH_3$	29.5	3.2	9.9			3.8
$OC(NH_2)NHC_6H_5$	161	14.8	8.4			3.2
$OC(NHCH_3)_2$	33.6		[d]			[d]

[a]Observed % N-isomer = $10^2 \times k_{ON}/(k_s + k_{ON}) = 10^2 \times k_{ON}/k$(obs.); k(obs.) values taken from Tables III and IV. [b]The N-isomer product is all $(NH_3)_5CoNHCONRR'^{2+}$; no $(NH_3)_5CoNRCONHR'^{2+}$ was detected. [c]Observed % N-isomer = $10^2 \times k'_{ON}/(k_{OH} + k'_{ON})$. [d]O- to N-isomerization not observable (see text).

observed 3–8% linkage isomerization, and this seems at least 100-fold too large, given that the leaving group is an anion. These considerations lead to the conclusion that all reaction goes via the $(NH_3)_4(NH_2)CoOC(NH_2)_2^{3+}$ tautomer.

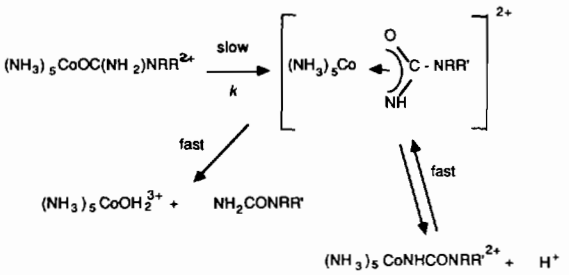
Spontaneous O- to N-linkage Isomerization

Precedent dictated that O- to N-linkage isomerization reactions, as against hydrolysis, would be more significant in acid solution, yet only aquation was observed (pH $\leqslant$ 2). This however proved to be a thermodynamic rather than a kinetic problem. The position of the urea-*O*/urea-*N* equilibrium is strongly pH dependent, favouring the O-isomer in acid and N-isomer in base. The equilibrium is governed by the relationship (*vide infra*)

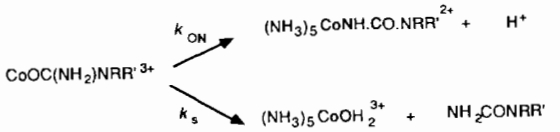
$$K'_{NO}(\text{obs.}) = \frac{K'_{NO}[H^+]}{K'_a + [H^+]}$$

For the unsubstituted urea system, K'_{NO}(obs.) = 240 at pH 1 and K'_{NO}(obs.) = 0.026 at pH 6. Thus essentially irreversible O- to N-isomerization can be observed only at pH $\geqslant$ 6. There was a further restriction on the observation of the spontaneous O- to N-rearrangement – the pH could not exceed ~7 without a significant contribution from the base-catalyzed pathway. Notwithstanding these restrictions, we found that spontaneous linkage isomerization could be observed clearly over a narrow pH region for the four urea-*O* complexes which possessed the *exo*-NH_2 group necessary for the rearrangement. For the pH 6.5 reaction, it was shown that the O- to N-isomerization pathway was irreversible by demonstrating that the product ratio $(Co(\text{urea-}N)^{2+}/CoOH_2^{3+})$ was independent of the extent of reaction (~1$t_{1/2}$ and >3$t_{1/2}$, *i.e.* 50–90% reaction), consistent with K'_{ON}(obs.) < 0.1. The product ratio was also independent of pH over the narrow range studied (~6.3–7.0, Table IV), consistent with a negligible contribution from the base-catalyzed reaction in this region. This is also apparent from the product distributions – there is much more urea-*N* product formed in the neutral pH region than at either high or low pH (Table IV).

The appearance of the additional reaction path, O- to N-linkage isomerization, as the pH is raised from 0 to 6, suggested a means of ascertaining whether hydrolysis and isomerization proceed via a common precursor, or whether they are separate processes. For a single rate determining step, the rate must be constant even while the product distribution varies with pH



For direct parallel paths there must be a rate increase commensurate with the increased contribution from the O- to N-isomerization



Thus at pH 1, k(obs.) = k_s while at pH 6, k(obs.) = $k_s + k_{ON}$. The rate data (Table III) show that the second scheme operates since the rate increases match well the extent of O- to N-rearrangement. This is clearest for the urea-*O* system; the 25% rise (pH 0

to 6) is well outside experimental error (k, ±3%). The data for $HClO_4$ and $NaClO_4$ media (μ = 1 M) show that the effect is not attributable to a change in supporting electrolyte.

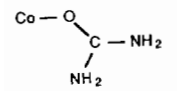
In a previous study [14], the rate profile showing the pH dependence of the hydrolysis rates of the unsubstituted urea-*O* species was analyzed for the region 6–14 (25 °C) using the equation

$$k(\text{obs.}) = k_s + \frac{k_{OH}K'_w}{K'_a + [H^+]}$$

The first term corresponds to the spontaneous path, and the second the base-catalyzed path but modified to accommodate deprotonation of the O-isomer in strong OH^-. The value of k_s so obtained (5.1×10^{-5} s^{-1}) was somewhat greater than that determined directly for strongly acid solution (4.0×10^{-5} s^{-1}). A similar but smaller disparity was noted in the later study [16] of the *N,N*-dimethylurea-*O* complex (3.8×10^{-5} *versus* 3.05×10^{-5} s^{-1}). The reason for the sense and magnitude of these differences is now clear; the measurements in acid give k_s while those for the extrapolated higher pH data yield $k_s + k_{ON}$.

These results demonstrate that linkage isomerization and the accompanying hydrolysis are separate reaction paths. An important corollary is that linkage isomerization is intramolecular – the urea moiety never leaves the metal ion.

From the rate data of Table III, it can be seen that the values for k_s are almost independent of the number and position of the *N*-methyl substituents, whereas the specific rates for the accompanying O- to N-isomerization span a factor of two. Given that a *cis*-NH_2 group seems to be a requirement for the latter process, it seemed reasonable to attempt to correlate the dependence of k_{ON} on R in terms of the probability of achieving the required conformation. The possibilities for the urea-*O* species in question are



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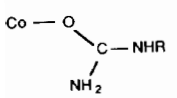

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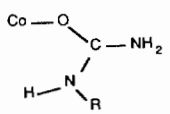

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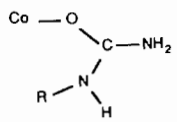

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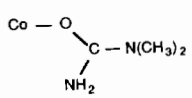

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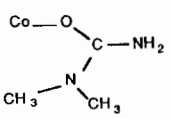


16

The relative rates (k_{ON}) should reflect the relative populations of conformer **14**. The species **16** are presumed to be sterically prohibited because of non-bonded interactions between the R group and the ammines of the $(NH_3)_5Co$ moiety; molecular models indicate this situation is not relieved by rotation about the Co–O bond. Thus, if conformers **14** and **15** are considered equal in energy, the relative rates of O- to N-rearrangement for the urea, Me_2N-urea and MeNH-urea species are predicted to be 3:3:2, respectively. The observed ratios (Table V) are 3:1.4:0.75, in poor agreement. However the agreement is improved if allowance is made for the different rates of Co–O cleavage across the series (reflected in k_s values). The corrected ratios become 3:2:1, and here we could add the anomalously reactive phenylurea-*O* complex, yielding 3:2:1:1 as against the 3:3:2:2 predicted. Clearly this analysis is far from compelling, although it seems to have qualitative merit.

In all cases the specific rate of O- to N-isomerization is smaller than that for the parallel hydrolysis by a factor of 3–5. This rate difference is accommodated by the probability of entry of H_2O or $-NH_2$ at a position adjacent to the leaving group (since substitution reactions of pentaamminecobalt(III) are stereoretentive in acid), indicating little difference in bond-making, if any, by the incoming nucleophile.

The final point concerns the greater importance of O- to N-rearrangement by the spontaneous (e.g. urea, 24.5%) as opposed to the base-catalyzed route (7.2%) (Table IV). This is a recurring feature of linkage isomerization amongst $(NH_3)_5CoX^{n+}$ complexes, and it has been argued that this reflects more associative character in the spontaneous process, compared with the base-catalyzed reaction where dissociative activation is promoted by the strongly labilizing aminate ion ($-NH_2^-$). However the effect is usually very pronounced, e.g. for $(NH_3)_5CoSCN^{2+}$, $k_{SN}/k_s > 50$ but $k'_{SN}/k_{OH} \sim 0.3$, corresponding to a $\geqslant$170-fold change in product distribution. For the present urea systems, there is only a 2- to 3-fold change. Since the $-NH_2$ must enter *cis* to the leaving group in the spontaneous process (because of the geometric retention), whereas for the base-catalyzed process the nucleophile enters *cis* and *trans* to the leaving group (because of the geometric rearrangement, *ca.* 50%), a two-fold change in the $(NH_3)_5Co$-(urea-*N*)$^{2+}$/$(NH_3)_5CoOH^{2+}$ product distribution is precisely the expectation if there were negligible associative activation for both the spontaneous and OH^--catalyzed reactions. This is in accord with the other facts, and we conclude that bond-making both by incoming H_2O and $-NH_2$ is negligible. Also this view is consistent with that generally accepted for dissociative activation in the hydrolysis reactions of $(NH_3)_5CoX^{n+}$, and that amine-like nitrogens are exceedingly poor nucleophiles towards cobalt(III).

Nitrosation

The urea-*O* complexes react with NO^+ to produce $(NH_3)_5CoOH_2^{3+}$, CO_2, N_2 and N_2O. Although this induced aquation is faster than spontaneous hydrolysis, it is much slower than the nitrosation of $(NH_3)_5CoO_2CNH_2^{2+}$ under the same conditions. Thus the expected carbamate-*O* intermediate was not observed, although the possibility that the urea-*O* complex nitrosates directly to give the aqua ion cannot be eliminated. We had hoped to generate $(NH_3)_5Co^{3+}$ by the above route and characterize it by way of established anion competition properties. Also, since such competition shows a small but definite dependence on the formal charge of the precursor complex, we had hoped to distinguish sequential from direct nitrosation of the urea-*O* species. Unfortunately the reaction is too slow to be useful in both respects. Ions such as $(NH_3)_5CoNCNH_2^{3+}$ and $(NH_3)_5CoOC(NH_2)(OCH_2CH_3)^{2+}$ are also slow to nitrosate, whereas 2+ species such as $(NH_3)_5CoN_3^{2+}$ react rapidly, and it seems electrophilic addition is inhibited by the increased positive charge on the complex.

$$(NH_3)_5CoOC(NH_2)^{3+} \xrightarrow{NO^+} (NH_3)_5CoO_2C(NH_2)^{2+} \xrightarrow{NO^+} (NH_3)_5CoOH_2^{3+}$$

At a pH sufficiently low to effect any reaction, the amide-*N* complexes were found to isomerize to their O-bonded forms, via the protonated forms $(NH_3)_5CoNH_2CONRR'^{3+}$ (*vide infra*).

Linkage Isomerization and Solvolysis Reactions of the Urea-N Complexes

All the urea-*N* species are stable indefinitely in solution as their crimson deprotonated forms, $(NH_3)_5CoNHCONRR'^{2+}$. They decompose only slowly even in strong aqueous OH^- (0.1–1.0 M), yielding some cobalt oxide. However the rearrangement rate of the N-bonded urea complexes becomes significant as the pH is lowered. Half-lives of several hours are observed at pH ~ 7 (25 °C) but several minutes near and below pH ~ 3. These observations are accommodated by an acid–base preequilibrium comprising the conjugate acid ($pK'_a \sim 3$) as the reactive species

$$(NH_3)_5CoNHCON(CH_3)_2^{2+} + H^+ \rightleftharpoons (NH_3)_5CoNH_2CONRR'^{3+} \xrightarrow{k + k_{NO}} \text{products}$$

leading to the rate law $-d[\text{complex}]/dt = \{(k + k_{NO})K'[H^+]/(1 + K'[H^+])\}[Co] = k(\text{obs.})[\text{complex}]$. The rate becomes independent of acid when $K'[H^+] \gg 1$, *i.e.* pH ≤ 2, since $K' = 1/K'_a \approx 10^3$; under these conditions $k(\text{obs.}) = k_{NO}$.

We have measured the specific rates k_{NO} for the N-bonded unsubstituted urea and two methylated derivatives, in both H_2O and Me_2SO in the presence of excess acid (0.1 and 1.0 M $[HClO_4]$, μ = 1.0 M ($NaClO_4$); 0.1 M for Me_2SO).

In this strong acid region the specific rates are independent of acid (Table VI), as found for the *N,N*-dimethylurea complex, and clearly there is no further protonation (at oxygen or at the *exo*-amine substituent), beyond the $(NH_3)_5CoNH_2CONRR'^{3+}$ stage. Although values of K'_a were not determined for all the $(NH_3)_5Co(\text{urea-}N)^{3+}$ species, all were fully protonated at the 0.1 M $[H^+]$ level in H_2O and Me_2SO, and fully deprotonated in H_2O at pH 5, *i.e.* pK'_a 2–4. A similar narrow range of pK'_a values (<2 units) pertains for the substituted amide-*N* complexes, $(NH_3)_5Co(NH_2COR)^{3+}$. Also we note that pK'_a values for a particular amide-*N* species are similar for H_2O and Me_2SO, and this seems to be true also of the urea-*N* complexes.

The essential reaction of the urea-*N* species in acid solution is linkage isomerization, accompanied by some (≤10%) direct solvolysis

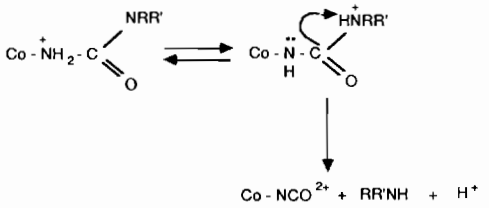
$$(NH_3)_5CoNH_2CONRR'^{3+} \xrightarrow{k_{NO}} (NH_3)_5CoOC(NH_2)NRR'^{3+}$$
$$(NH_3)_5CoNH_2CONRR'^{3+} \xrightarrow{sol,\ k} (NH_3)_5Co(sol)^{3+} + NH_2CONRR'$$

Neither $(NH_3)_6Co^{3+}$ (arising from CoN–C cleavage) nor $(NH_3)_5CoO_2C(NH_2)^{2+}$ (CoNC(O)–N cleavage) were detected (<0.5%) in chromatographic experiments devised to optimize their detection. Either of these products could arise by H_2O attack at the carbonyl center.

$$\text{Co-NH}_2\text{-C(=O)-NRR'} \xrightarrow{H_2O} \text{Co-NH}_2\text{-C(OH)(OH)-NRR'}$$
$$\text{Co-NH}_2\text{-C(OH)(OH)-NRR'} \rightarrow \text{Co-NH}_3^{3+} + CO_2 + HNRR'$$
$$\text{Co-NH}_2\text{-C(OH)(OH)-NRR'} \rightarrow \text{Co-O}_2\text{CNH}_2^{2+} + H^+$$
$$\text{Co-NH}_2\text{-C(OH)(OH)-NRR'} \rightarrow \text{Co-NH}_2\text{COOH}^{3+} + HNRR'$$

Centainly the Co(III) center should activate the urea-*N* moiety towards hydrolysis, but the activation is insufficient to compete with the facile urea-*N* to urea-*O* linkage isomerization reaction which is observed ($t_{1/2}$ ~ min, 25 °C). Also we note that the $(NH_3)_5CoNCO^{2+}$ ion was not observed (<0.5%); the cyanate-*N* complex leads to largely $(NH_3)_6Co^{3+}$ in aqueous acid but is stable in Me_2SO/H^+. The cyanate

complex can arise by Co(III)-activated elimination



This pathway has been observed when the urea-*N* complex has a leaving group which is sufficiently good ($-NH_2C_6H_5$) [29], or when the competitive N- to O-linkage isomerization is sufficiently slow (Rh(III)–NH_2CONH_2) [19a].

The stoichiometry of the urea-*N* reaction in acid solution was established in several ways. The reaction in Me_2SO-d_6/H^+ was followed by both ^1H and ^{13}C NMR spectroscopy. Signals attributable to the protonated N-bonded isomer were replaced rapidly by those for the O-bonded isomer, together with weaker resonances (5–10%) attributable to the free urea ligand arising from solvolysis. The *exo*-NH_2 signals for O-coordinated urea (^1H NMR) were broadened somewhat in the presence of excess H^+. Also, the $-NH_2$ signal for the free urea ligand was not observed. The latter is exchange-averaged with free H^+ and traces of H_2O present in the Me_2SO-d_6, as shown in control experiments. Subsequently, and much more slowly, the intensity of the free urea signals increased at the expense of those attributed to the O-bonded isomer. The signal assignments were confirmed in separate experiments by adding authentic specimens of the O-bonded isomer and free ligand to the reacting solution. Also, the specific rates measured for this second slow step coincided exactly with those independently determined for the O-bonded isomers. While this merely establishes that at least some O-bonded isomer is formed, the isolation of the O-bonded isomers in >90% yield from the reaction of the N-bonded isomers in acid solution (H_2O or Me_2SO) indicates that linkage isomerization is the predominant process.

The stoichiometries for the reactions of the *N,N*-dimethylurea-*N* and urea-*N* complexes were confirmed using ion-exchange chromatography. These ions were reacted for 10 $t_{1/2}$ in H_2O (0.1 M in H^+) at 25 °C and the products immediately chromatographed on Dowex at ~2 °C. The pink O-bonded isomers were separated from orange $(NH_3)_5CoOH_2^{3+}$ using a Cl^-/phosphate (pH 7) eluent, and the [Co] determined spectrophotometrically. The product proportions were corrected for some solvolysis of the O-bonded isomers which occurs in the time required to completely react the corresponding N-bonded isomers, using the specific rates recorded in Tables III and VI. No significant reaction (≤1%) occurs during the actual ion-exchange separation at 2 °C (~2 h). The results of these analyses (Table VII) confirm that some direct solvolysis accompanies the linkage isomerization reaction, albeit small. The observed specific rates *k*(obs.) have been subdivided to give individual values

TABLE VI. Specific Rates and Activation Parameters for the N- to O-linkage Isomerization Reactions of $(NH_3)_5CoNH_2CONRR'^{3+}$

Ligand	H_2O [a, b]		Me_2SO [b, c]	
	T (°C)	$10^4 \times k$(obs.) (s^{-1})	T (°C)	$10^4 \times k$(obs.) (s^{-1})
NH_2CONH_2	19.7	17.4 ± 0.5	20.6	4.67 ± 0.14
	25.0	34.9 ± 1.0	25.0	8.9 ± 0.27
	29.2	58.7 ± 1.3	29.0	16.7 ± 0.5
	35.5	117.0 ± 5.0	35.3	34.2 ± 1.5
	$\Delta H^{\neq}$	89.1 ± 2.1 kJ mol^{-1}	$\Delta H^{\neq}$	101.7 ± 4.6 kJ mol^{-1}
	$\Delta S^{\neq}$	7.0 ± 7.1 J mol^{-1} K^{-1}	$\Delta S^{\neq}$	37.2 ± 15.5 J mol^{-1} K^{-1}
$NH_2CONHCH_3$	25.0	14.7 ± 0.6		
$NH_2CON(CH_3)_2$	20.4	115.0 ± 5.0	20.4	66.3 ± 2.0
	25.0	179.0 ± 10.0	25.0	114.0 ± 7.0
	29.4	299.0 ± 12.0	29.4	216.0 ± 11.0
	29.7	305.0 ± 12.0	29.7	220.0 ± 10.0
	35.5	580.0 ± 22.0	35.5	441.0 ± 14.0
	$\Delta H^{\neq}$	78.7 ± 2.4[d] kJ mol^{-1}	$\Delta H^{\neq}$	92.5 ± 1.6 kJ mol^{-1}
	$\Delta S^{\neq}$	−13.8 ± 7.9 J mol^{-1} K^{-1}	$\Delta S^{\neq}$	28.5 ± 5.4 J mol^{-1} K^{-1}

[a]μ = 1.2 M ($HClO_4$) except for dimethylurea, μ = 0.1 M ($HClO_4$). [b]Individual entries are the means and standard deviations for three or more determinations. [c]Added CF_3SO_3H (~3 equiv.); [Co] ~ 5×10^{-3} M. [d]Weighted least-squares analysis of the data given in ref. 16 for the 0.5 M HCl/0.5 M KCl medium yields $\Delta H^{\neq}$ = 82.0 ± 8.2 kJ mol^{-1}, and $\Delta S^{\neq}$ = −4.4 ± 2.8 J mol^{-1} K^{-1}.

TABLE VII. Specific Rates for N- to O-linkage Isomerization and Aquation of the $(NH_3)_5Co(urea\text{-}N)^{3+}$ Complexes, and Data for the Urea-*N*/Urea-*O* Equilibrium; μ = 1.0 M, 25 °C

Ligand	$10^4 \times k$(obs.) (s^{-1})	Isomerization[a] (%)	$10^4 \times k_{NO}$[b] (s^{-1})	$10^4 \times k$[c] (s^{-1})	K'_{NO}[d]
NH_2CONH_2	34.9	90.4	31.5	3.4	246
$NH_2CONH(CH_3)$	14.7	87.0	12.8	1.9	400
$NH_2CON(CH_3)_2$	179	95.0	170	9.0	2830
$NH_2CONH(C_6H_6)$	[e]	[e]	23.9	9.5	161

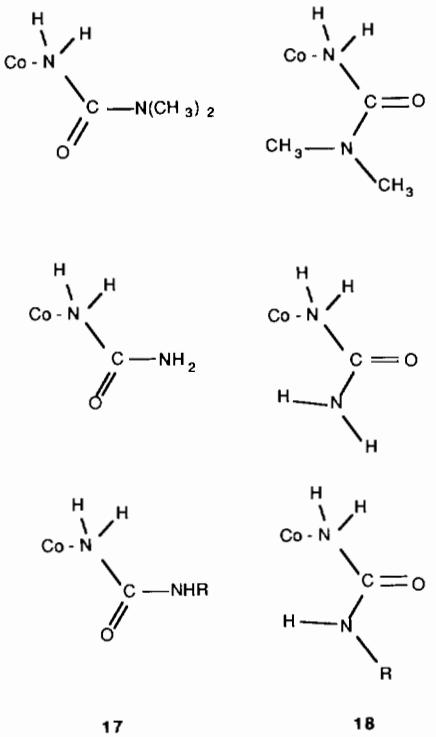
[a]The minor reaction is hydrolysis leading to $(NH_3)_5CoOH_2^{3+}$ and free ligands; these data have been corrected for subsequent reaction of the O-bonded isomers which occurs during N- to O-isomerization and the chromatographic work up (~2 h at 2 °C). [b]Specific rate of N- to O-linkage isomerization. [c]Specific rate of aquation. [d]Equilibrium constant for the urea-N^{3+}/urea-O^{3+} reaction, calculated from k_{NO}/k_{ON}; k_{ON} values from Table V. [e]The phenylurea-*N* complex reacts by multiple pathways [27].

for k_{NO} and k, using the appropriate product ratios determined for each of these parallel reactions (Table VII). Note that the specific rates of solvolysis k are not especially accurate because of the minor contribution from this path; an error of at least ±20% is estimated.

The specific rates of linkage isomerization k_{NO} vary with the substitutions on the *exo*-amine. In H_2O, the spread in rates is ~5-fold, and in Me_2SO ~13-fold at 25 °C. The rates do not vary systematically with methyl-substitution. The *N,N*-dimethylurea complex is the fastest in each solvent, yet in H_2O the next fastest is not the *N*-methylurea but rather the unsubstituted urea species. Finally, the effect of solvent is consistent but not great. Rates for the two urea systems are lower in Me_2SO compared to H_2O, by factors of 1.5 and 3.9, respectively, at 25 °C. Much the same situation pertains at temperatures in the range 20–35 °C. Not surprisingly, the activation parameters (Table VI) are not very different, and no real significance could be attached to an explanation to accommodate these differences.

The observation of parallel formation of O-bonded isomer and solvolysis product has significance. First, it shows clearly that the N- to O-linkage isomerization occurs intramolecularly, and not via $(NH_3)_5Co(sol)^{3+}$ which is then rapidly substituted by the liberated free urea. It was shown earlier that the O-bonded isomer aquates irreversibly; moreover, substitution rates for $(NH_3)_5Co(sol)^{3+}$ are far too slow for this to be a tenable alternative. Furthermore we have shown that, under favourable thermodynamic conditions, the O-bonded isomer isomerizes directly to the N-bonded form, and that the competitive solvolysis path is a distinctly separate reaction pathway. It follows from the principle of microscopic reversibility that the reverse N- to O- process is concerted also, in the sense that it is separate from the solvolysis path.

The relative rates of linkage isomerization can be accommodated by a conformational argument similar to that advanced for the O-bonded isomer reactions



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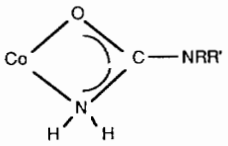
If a *cis*-oxygen is required for N- to O-rearrangement (conformer **17**), then the rate for the dimethylurea derivative (the fastest) suggests that **17** is adopted for this system, while for the others which are less sterically demanding there will be contributions from **18**. This analysis assumes that a common mechanism operates and that methyl-substitution does not greatly affect the Co–NH_2 bond strength. Some evidence for the latter may be adduced from the specific rates for the parallel hydrolysis (k, Table VII), since these should not be so dependent upon the conformation. The results indicate some dependence of k on the substituents of the urea (as found for the O-bonded isomers, Table III), but there are no

consistencies within or between the urea-*O* and urea-*N* aquation rate data. The important point is that the variation in k_{NO} is large (~13-fold), while smaller for k (<4-fold).

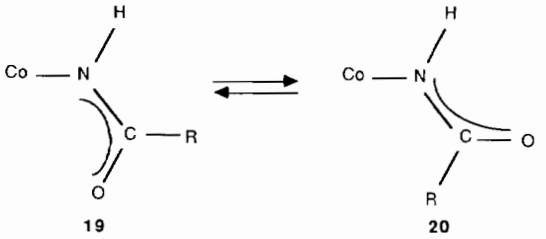
The more striking feature of the data is the much faster rate of N- to O-linkage isomerization compared to hydrolysis – up to 20-fold. We interpret this as some bond-making by the incoming carbonyl oxygen, *i.e.* some associative character to the rearrangement process (the aquation reactions of $(NH_3)_5CoX^{n+}$ are generally agreed to be dissociative). This conclusion is not in conflict with the assignment of a predominantly dissociative mechanism for the reverse O- to N-linkage isomerization process. Rather, the investigations on both the forward and reverse reactions jointly point to a (common) transition state in which Co–O bonding remains significant while Co–N bonding is very weak



Indeed, the bonding in the transition state for the urea-*N* to urea-*O* rearrangement possibly reflects the major factor which determines the relative stability of the two isomers. In water and Me_2SO, the N-bonded isomer is at least 9 kJ mol^{-1} less stable (see next section), indicating that the Co–O bond is stronger than Co–N for the urea ligands.

Work on the analogous amide-*N* systems [17] has provided results germaine to the present discussion. As with the ureas, the $(NH_3)_5CoNHCOR^{2+}$ ions protonate in strong acid and the resultant species linkage isomerize with parallel solvolysis. But the urea and amide systems differ in three important respects. First, the urea-*N* complexes protonate on nitrogen (for Me_2SO at least), while the amide-*N* analogues protonate on oxygen. Second, the N- to O-rearrangement rates for the ureas span a factor of about 10, but as a class they are significantly faster (~100-fold) to isomerize than the amide-*N* complexes. Third, the accompanying solvolysis is much more prominent in the amide systems.

The faster N- to O-isomerization rates for the urea systems might be taken to suggest that the conformer distribution for the amides is different, with a higher population of **20**. Again, conformer **19** having the *cis*-oxygen is assumed to be the reactive species. However, while the **19**/**20** conformer distribution can account for the R dependence of the small spread of rates observed within the amide-*N* systems, this explanation fails on two counts to accommodate the generally much greater urea-*N* rates. In fact, the conformer distribution is known for $(NH_3)_5CoNHC(OH)$-

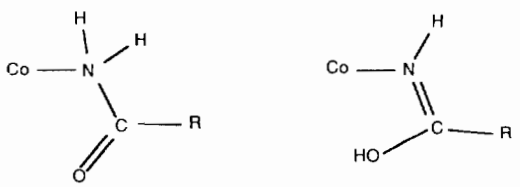


19 **20**

H^{3+} (~1:1) [17], yet the specific rate for N- to O-isomerization is well below that for $(NH_3)_5CoNH_2$-$CON(CH_3)_2^{3+}$ (~100-fold), which is likely to exist entirely as conformer **19**. Only a two-fold rate difference would be expected if the accessibility of conformer **19** was the only consideration. Furthermore the R dependence of the amide-*N* rates and NMR identification of $(NH_3)_5Co(amide\text{-}N)^{3+}$ suggest that conformer **19** is strongly favoured for bulky R, yet even these complexes linkage isomerize slowly relative to the ureas.

A clue to the difference in mechanism between the urea-*N* and amide-*N* rearrangements comes from a consideration of the hydrolysis rates for the competitive hydrolysis reaction. These results suggest that the Co–N bond is somewhat stronger for the amide systems. However this factor alone cannot accommodate a slower N- to O-rearrangement rate for the amides. A residual enhanced reactivity for the urea-*N* to urea-*O* process (~20-fold) is evident in the k_{NO}/k ratios, ~20 for the ureas and ~1 for the amides. This can be interpreted as more associative character to the urea-*N* to urea-*O* rearrangements in comparison with the amides, and this difference in mechanism can be understood from the solution structures. The N-protonated urea species **21** permit a shorter Co–O distance in the ground state. This follows from the expected bond angles (CoNC), ~109° for the ureas **21** and ~120° for the corresponding amide species **22**. Given that the *cis* conformation is required for the N- to O-rearrangement, this closer proximity should facilitate Co–O bond making in the transition state. Also the oxygen of the urea-carbonyl, bearing a partial negative charge, may be a better nucleophile than the amide-OH.

The amide tautomer **22** may even be less reactive than the observed rates suggest, and it is possible that the amides and ureas both rearrange via the



21 **22**

N-protonated tautomer **21**, with the slower amide rates reflecting the higher population of the inactive **22**. If this is so, then both **22** and **21** must hydrolyze at comparable rates to accommodate the variation in k_{NO}/k, and this seems plausible.

The $(NH_3)_5Co(urea\text{-}N)^{3+}/(NH_3)_5Co(urea\text{-}O)^{3+}$ Equilibrium

This equilibrium was of interest in the general context of the relative stability of linkage isomeric metal complexes. Most thermodynamic data refer to M-SCN/M-NCS systems, but results for a broader range of linkage isomeric pairs are now appearing.

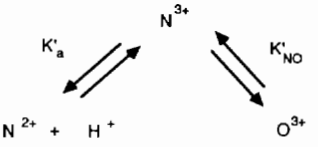
A fundamental problem in obtaining equilibrium constant data is the fact that linkage isomers often differ in energy by $\geqslant$10 kJ mol^{-1}. Thus the equilibrium lies so far to one side that most techniques cannot reliably measure or even detect the minor isomer. Another difficulty is the solvolysis side-reaction in coordinating solvents which precludes direct measurement of the equilibrium constant.

For the N- and O-bonded urea systems, these difficulties have been circumvented by utilizing the stability of the urea-*N* species as its deprotonated form in base. Thus, while in acid solution the N- to O-rearrangement proceeds to completion, the reverse O- to N-isomerization can also be forced to completion. Hydrolysis accompanies both the forward and reverse reactions, but we have confirmed the irreversibility of the rearrangements under the two sets of conditions by observing product ratios which do not change in the time required for complete reaction of the starting isomer.

The equilibrium constants K'_{NO} were calculated as k_{NO}/k_{ON} using the independently determined rate constants (Table VII). The results for water reflect a much greater stability for the O-bonded isomer in each case, by 11–20 kJ mol^{-1}. Since K'_{NO} is inextricably related to k_{NO} and k_{ON}, the variation in K'_{NO} with the urea substituent can be ascribed to the conformational preference of the N- and O-bonded isomers, and including a statistical factor of two for the unsubstituted urea system. The dimethylurea system, K'_{NO} = 2830, is probably best representative of the inherent enthalpy difference between the urea isomers, since each likely exists as a single conformer; the other effects should appear in the entropy term. Also we note the K'_{NO} for the urea isomer equilibrium involving coordination of the monosubstituted nitrogen is undoubtedly $\geqslant 10^3$; Co–N(R)–bonding could not be forced even in non-coordinating solvents containing base, conditions which result in complete O- to N-rearrangement when resultant Co–NH= coordination is involved.

Equilibrium data for Me_2SO could not be obtained, but it was clear that $K'_{NO} > 10^2$ in each case since no (<1%) N-isomer could be detected at 10 $t_{1/2}$ of the N- to O-rearrangement.

The equilibrium data analysis is justified as follows



For this system

$$K'_{NO}(\text{obs.}) = [O^{3+}]/([N^{3+}] + [N^{2+}])$$
$$= K'_{NO}[H^+]/([H^+] + K'_a)$$

where N^{3+}, N^{2+} and O^{3+} denote the protonated, deprotonated urea-*N* and urea-*O* species respectively, and K'_{NO}(obs.) is the equilibrium isomer distribution defined as [O-isomer]/[total N-isomer]. The acidity constant K'_a is known for the *N,N*-dimethylurea-*N* species, $10^{-2.9}$ (1 M KCl, 25 °C). Using this value for the unsubstituted urea species, and the K'_{NO} result we calculate K'_{NO}(obs.) = 241, at pH 1; K'_{NO}(obs.) = 0.039, at pH 6.5; K'_{NO}(obs.) = 1.2×10^{-5}, at pH 10; for this system. This is consistent with our observations that the urea equilibrium lies essentially fully to the side of the N-bonded isomer in neutral to basic solution but fully to the side of the O-bonded isomer below pH ~1.

The Co(III)–NH_2CONH_2 system may be contrasted with its direct Rh(III) analog [19a] for which $K'_{NO} \sim 1$, and clearly there is less preference for O-bonding over N-bonding in the Rh(III) system. This contrast is consistent with other chemistry where in general, compared to the smaller Co(III), softer N-bonding ligands such as amines bond more strongly to the larger (softer) Rh(III) metal ion. This argument cannot be pushed too strongly however because, even for Co(III), O-binding ligands are not uniformly preferred to those which bind through N. The sulfamate $(NH_3)_5Co(sulfamate)^{2+}$ ion, for example, exists as a ~3:1 equilibrium mixture of the N- and O-bonded isomers largely because sulfonate oxygen is not an especially good ligand towards Co(III), while in contrast, for $Co(NH_3)_5(NO_2)^+$ the equilibrium between the nitrito (O-) and nitro (N-) forms lies fully to the side of the N-bonded isomer.

Experimental

Visible spectra (λ, nm; ϵ, M^{-1} cm^{-1}) were recorded with Cary 118C and 210 instruments with modified cell blocks thermostated at 25.0 ± 0.1 °C by water circulation from an external Lauda bath. Cation-exchange media were SP-Sephadex C25 (Pharmacia) and Dowex 50WX2 (H^+ or Na^+ form, 200–400 mesh; Biorad). Proton NMR spectra were recorded with a Varian T60 instrument at ~35 °C. Carbon-13 NMR spectra were obtained from a Jeol 90FXQ

spectrometer at ~30 °C. Me_2SO-d_6 was generally the solvent, and chemical shifts are reported as positive downfield from tetramethylsilane. Dioxane (66.26 ppm) was used as the internal reference for the ^{13}C NMR spectra. Chemicals were analaR grade or the equivalent. All new complexes analyzed satisfactorily for C, H, N and either S (dithionate salts) or Cl (perchlorate salts). Known complexes were characterized by comparison of their spectroscopic properties (NMR and Vis–UV) with the literature data.

Synthesis of O-bonded Isomers

A variation of a published method [14b] used to prepare $[(NH_3)_5CoOC(NH_2)_2]_2(S_2O_6)_3\cdot 3H_2O$ was employed also to synthesize $[(NH_3)_5CoOC(NH_2)(N(CH_3)_2)]_2(S_2O_6)_3\cdot 3H_2O$ [16], $[(NH_3)_5CoOC(NHCH_3)_2]_2(S_2O_6)_3\cdot 3H_2O$, $[(NH_3)_5CoOC(NH_2)(NHCH_3)]_2(S_2O_6)_3\cdot 3H_2O$ and $[(NH_3)_5CoOC(NH_2)(NHC_6H_5)]_2(S_2O_6)_3\cdot 3H_2O$. To a solution of the urea (5 g) in acetone (AR, 50 ml) was added with stirring $[(NH_3)_5CoO_3SCF_3](CF_3SO_3)_2$ (5 g). The mixture was warmed to ~60 °C (15 min) to complete the reaction, and then poured into butan-2-ol (30 ml). The addition of ether (100 ml) then yielded a thick red oil which solidified within minutes on stirring. This was rapidly dissolved in a minimum of ice-water, filtered, and treated with a fifth-volume of saturated aqueous $Na_2S_2O_6$ at 20 °C. On cooling and stirring, fine pink needles deposited. These were collected after 1 h at 0 °C, washed with ice-water (3 × 30 ml), ethanol (2 × 30 ml), ether (2 × 30 ml), and finally air-dried. Yield: ~85%. The ClO_4^- salts were obtained from the purified dithionates as previously described [16].

Synthesis of N-bonded Isomers

$[(NH_3)_5CoNHCONH_2](ClO_4)_2\cdot H_2O$, $[(NH_3)_5CoNHCONHCH_3](ClO_4)_2\cdot H_2O$, $[(NH_3)_5CoNHCON(CH_3)_2](ClO_4)_2\cdot H_2O$ and $[(NH_3)_5CoNHCONHC_6H_5](ClO_4)_2\cdot H_2O$ were prepared by the following method for the urea complex. To a solution of $[(NH_3)_5CoOS(CH_3)_2](ClO_4)_3\cdot H_2O$ (5 g) and urea (5 g) in Me_2SO (25 ml) was added 2,2,6,6-tetramethylpiperidine (3 g; Fluka, AG), and the mixture was heated (60 °C, 4 h). An oil was produced from the product mixture by pouring into butan-2-ol (75 ml) and adding ether (300 ml). The solid which resulted on stirring (30 min) was, after decantation, dissolved in water (30 ml) containing tris(aminoethyl) methylamine (tris; 0.01 M), filtered, and treated with a fifth-volume of saturated aqueous $NaClO_4$. After cooling, fractions were removed at intervals by filtration; the first (small) contained a little yellow hexaamminecobalt(III) and was discarded. The bulk of the material crystallized as the crimson–pink stoichiometric triflate/perchlorate salt, $[(NH_3)_5CoNHCONH_2]CF_3SO_3\cdot ClO_4\cdot H_2O$. Recrystallization from aqueous tris using $NaClO_4$ as the precipitant yielded the 2-perchlorate in reasonable overall yield. Lattice water was removed by prolonged drying over P_2O_5 *in vacuo*. Yields: 50–60%. The *N,N*-dimethyl derivative was also prepared by OH^- addition to $(NH_3)_5CoNCN(CH_3)_2^{3+}$ [16]; the yield here is essentially quantitative. The spectroscopic properties of the *N,N*-dimethylurea complex prepared by both routes were identical. It was usually more convenient to obtain the pure product after chromatographing the product mixtures on Sephadex, eluting with 0.3 M $NaClO_4$ (pH 9, tris) to separate the deprotonated N-bonded urea species from the slower moving ions $(NH_3)_5CoOH^{2+}$ and $(NH_3)_6Co^{3+}$.

The protonated urea-*N* isomers could be crystallized as yellow plates by dissolving the deprotonated forms in a minimum volume of cold 5 M HCl, and adding concentrated HNO_3. They were not characterized beyond noting that the deprotonated forms could be recovered quantitatively with use of base, and even washing of the crystalline solids with ethanol resulted in partial deprotonation. Washing with copious quantities of ether was effective, without deprotonation, but the resultant solids nonetheless isomerized in the solid state to the O-bonded forms at a rate precluding their convenient storage.

Product Analyses: Reactions of the O-bonded Isomers

(a) Base hydrolysis. Each of the five complexes $[(NH_3)_5Co(urea\text{-}O)]_2(S_2O_6)_3\cdot 3H_2O$ (0.5–0.8 g) was reacted (5 min, 25 °C) with 0.1 M NaOH (80 ml, μ = 1.0 M, $NaClO_4$), quenched with NH_4Cl (1 g), sorbed onto Dowex (Na^+) and eluted with 0.9 M NaCl/0.1 M sodium phosphate (pH 6.88). $(NH_3)_5Co(urea\text{-}N)^{2+}$ products eluted well ahead of $(NH_3)_5CoOH_2^{3+}$ and their proportions were quantified according to the absorption spectra of column eluates using ϵ_{492}(max) 47.7 ($(NH_3)_5CoOH_2^{3+}$, 1.0 M HCl), ϵ_{492}(max) 50.5 ($(NH_3)_5CoOH_2^{3+}$, 0.9 M NaCl/0.1 M sodium phosphate, pH 6.88), ϵ_{500}(max) 92 ($(NH_3)_5CoNHCONH_2^{2+}$), ϵ_{502}(max) 91 ($[(NH_3)_5CoNHCONHCH_3]^{2+}$), ϵ_{506}(max) 114 ($(NH_3)_5CoNHCON(CH_3)_2^{2+}$), ϵ_{500}(max) 116 ($(NH_3)_5CoNHCONHC_6H_5^{2+}$). Note that these numbers slightly differ from those listed in Table VIII because the media are different. No N-bonded isomer was produced from $(NH_3)_5CoOC(NHCH_3)_2^{3+}$.

(b) Hydrolysis at neutral pH. The five complexes $[(NH_3)_5Co(urea\text{-}O)]_2(S_2O_6)_3\cdot 3H_2O$ (0.5–0.8 g) were separately reacted with aqueous 0.1 M NaMES buffer (pH 6.2; μ = 1.0 M, $NaClO_4$) for 3 and 20 h at 20 °C, quenched with ice, chromatographed at 2 °C using jacketed columns of Sephadex, eluted and quantified as above. In each case three complexes were observed and identified as $(NH_3)_5Co(urea\text{-}N)^{2+}$, $(NH_3)_5CoOH_2^{3+}$ and $(NH_3)_5Co(urea\text{-}O)^{3+}$, eluted in that order, but no N-bonded isomer was formed from $(NH_3)_5CoOC(NHCH_3)_2^{3+}$.

TABLE VIII. Visible Spectral Data for $(NH_3)_5Co(urea\text{-}O)^{3+}$ and $(NH_3)_5Co(urea\text{-}N)^{2+/3+}$ Complexes

	λ_{max} (nm) (ϵ (M^{-1} cm^{-1}))	Solvent
$[(NH_3)_5CoOC(NH_2)_2]^{3+}$	519 (78.7); 352 (59.3)	a
$[(NH_3)_5CoOC(NH_2)(NHCH_3)]^{3+}$	520 (79.9); 346 (67.7)	a
$[(NH_3)_5CoOC(NH_2)(N(CH_3)_2)]^{3+}$	523 (93.5)	a
$[(NH_3)_5CoOC(NHCH_3)_2]^{3+}$	521 (84.1); 346 (77.9)	a
$[(NH_3)_5CoOC(NH_2)(NHC_6H_6)]^{3+}$	522 (86.4)[29]	a
$[(NH_3)_5CoNHCONH_2]^{2+}$ [e]	498 (90.4); 350 (125); 267(sh) (897)	b
$[(NH_3)_5CoNHCONH_2]^{2+}$ [f]	499 (88.3); 350 (125.9)	b
$[(NH_3)_5CoNH_2CONH_2]^{3+}$	485 (89.6); 349 (88.2)	a
$[(NH_3)_5CoNHCO(NHCH_3)]^{2+}$	501 (89.0); 350 (166); 284 (752)	b
$[(NH_3)_5CoNH_2CO(NHCH_3)]^{3+}$	487 (88)	a
$[(NH_3)_5CoNHCO(N(CH_3)_2)]^{2+}$ [e]	509 (114)	b
$[(NH_3)_5CoNHCO(N(CH_3)_2)]^{2+}$ [g]	509 (110.9); 375(sh) (219)[16]	c
$[(NH_3)_5CoNH_2CO(N(CH_3)_2)]^{3+}$	487 (69)	a, d
$[(NH_3)_5CoNHCO(NHC_6H_5)]^{2+}$	500 (121.0)[29]	b

[a]0.1 M $HClO_4$, μ = 1.0 M ($NaClO_4$). [b]0.1 M tris. [c]0.1 M HCl/$N(C_2H_5)_3$. [d]0.5 M HCl/0.5 M KCl. [e]2-Perchlorate salt. [f]Triflate/perchlorate salt. [g]2-Triflate salt.

(c) Acid hydrolysis and Me_2SO solvolysis. The dithionate salt of each O-bonded isomer was dissolved in 0.1 M $HClO_4$ or Me_2SO, and the resultant solutions were aged for $10t_{1/2}$ (Table III). The products were cooled, chromatographed at 2 °C and analyzed as in (a) above. No N-bonded isomers were detected (>1%), and the formation of $(NH_3)_5CoOH_2^{3+}$ or $(NH_3)_5CoOSMe_2^{3+}$ was quantitative. The latter ion was measured as the aqua species by treatment with base (0.1 M, 1 min) followed by acid (0.1 M $HClO_4$).

(d) Nitrosation. $[(NH_3)_5CoOC(NH_2)_2]_2S_2O_6 \cdot 3H_2O$ (1.4 mmol) was mixed with $NaNO_2$ (1.46 mmol) in water (10 ml, 21 °C) before acidifying (1.17 M $HClO_4$, 70 ml) and stirring (10 min, 21 °C), quenching in ice, sorption on and elution from Sephadex (Na^+) resin with 0.23 M Na^+ (pH 7, 0.01 M $H_2PO_4^-$, 0.01 M HPO_4^{2-}, 0.2 M Cl^-) eluant followed by a similar eluant at twice the concentration. Identification and quantitation by visible absorption spectra gave 2% $(NH_3)_5CoNO_2^{2+}$, 13% $(NH_3)_5CoOH_2^{3+}$ and unreacted O-bonded isomer (85%). Using 4.5 molar equivalents of $NaNO_2$ over 40 min (20 °C) resulted in the same products but in the ratio 7:18:75.

Hydrolysis of $[(NH_3)_5CoO_3SCF_3](CF_3SO_3)_2$ in 1.0 M Aqueous Urea

Samples of the trifalto complex (0.3–0.5 g) were dissolved in aqueous NaMES which was 1 M in urea (50 ml, 0.1 M, pH 6.3) at ambient temperature. After 10 $t_{1/2}$ (*ca.* 5–10 min), the mixture was cooled, diluted with ice water and sorbed on and eluted from an ice-jacketed Sephadex column. The products were eluted and identified as in (b) above; only the aqua complex was observed, under conditions where N- or O-bonded isomer if formed would survive the conditions and would be readily separated.

Product Analyses: Reactions of N-bonded Isomers

(a) Acid hydrolysis/isomerization. The four complexes $[(NH_3)_5Co(urea\text{-}N)](ClO_4)_2 \cdot H_2O$ (0.3–0.6 g) were each reacted with $HClO_4$ (1.17 M, 40 ml) for 10 $t_{1/2}$ (7–40 min, 25 °C; Table VII), cooled in ice, sorbed on and eluted from ice-jacketed columns of Sephadex with 0.46 M Na^+ (pH 7, 0.02 M $H_2PO_4^-$, 0.02 M HPO_4^{2-}, 0.4 M Cl^-) eluant. The first band (3+ ion) was acidified with HCl (1 M) to pH ~ 2 and identified spectrally as $(NH_3)_5CoOH_2^{3+}$. The second pinker band (3+) was similarly identified as the O-bonded urea isomer (Table VIII), and also measured as $(NH_3)_5CoOH_2^{3+}$, after treatment with 1 M NaOH (pH > 12, 10 min) followed by 3 M HCl (pH ~ 2). The product distribution results were corrected for some subsequent aquation of the O-bonded isomers which occurs in the time required to completely react the N-bonded isomers; the specific rates recorded in Tables III and VII were used for this purpose. For example, with $(NH_3)_5CoNH_2CONH_2^{3+}$ reacted at 19 °C for 46 min, we observed 84.9% $(NH_3)_5CoOC(NH_2)_2^{3+}$ and 15.1% $(NH_3)_5CoOH_2^{3+}$, which when corrected for aquation of the O-bonded isomer, became 89.2% $(NH_3)_5CoOC(NH_2)_2^{3+}$ and 10.8% $(NH_3)_5CoOH_2^{3+}$. Aquation during chromatography (1–2 h, 2 °C) was negligible.

Kinetic Studies

Rates for solvolysis (Table III) of $(NH_3)_5Co(urea\text{-}O)^{3+}$ ions in aqueous solution ($HClO_4$ and NaMES buffer) were measured (25 °C) relative to each other in a five-cell rotating thermostated compartment of the Cary 210 instrument, from absorbance/time traces at 520 nm. Specific rates of O- to N-isomerization and competiting aquation (Table VI) were obtained for those parallel paths by dividing the

observed rates according to the (corrected) product distributions (Table IV). Rates for reaction of $(NH_3)_5Co(urea\text{-}N)^{2+}$ ions in aqueous acid and acidic Me_2SO (Tables VI, VII) were determined from absorbance/time traces at 520 nm, and rates subdivided as above for parallel reactions. All absorbance/time data were fitted in the usual way by weighted non-linear least-squares analysis. The data closely followed a single exponential function over $\geqslant 3\ t_{1/2}$, and all reported rate constants represent averages of at least 3 determinations.

NMR Studies

The 60 MHz spectra were recorded for the 2-perchlorate salts of $(NH_3)_5CoNHCONH_2^{2+}$, $(NH_3)_5CoNHCONHCH_3^{2+}$, $(NH_3)_5CoNHCON(CH_3)_2^{2+}$ and $(NH_3)_5CoNHCONHC_6H_5^{2+}$ in Me_2SO-d_6, before and after adding acid. These solutions were cooled to or below the freezing point of the solvent before adding a molar excess of cold (<0 °C) concentrated acid (CF_3SO_3H, CH_3SO_3H, or CF_3CO_2H) dropwise, rapidly shaking the tube, and quickly and repeatedly recording spectra. Initial spectra were obtained by extrapolating the series obtained to zero time. As it happened, a range of initial temperatures (20–40 °C) were achieved by the above technique, and in this range the various stages of coalescence of the *exo*-NH_2 resonances for $(NH_3)_5CoNH_2CONH_2^{3+}$ were observed.

The major product (>90%) of reaction in Me_2SO was identified as the corresponding urea-*O* complex by comparison with the spectrum of an authentic specimen. This was also shown by ^{13}C NMR spectroscopy.

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