10.46, a rate of 0.13 is calculated at 60 °C from the amine buffer data. The corresponding rate for the 5-methyltetrazolato complex is calculated to be $3.1 \times 10^{-4}$ s$^{-1}$, and that of the $NO_2^-$ complex is $2.9 \times 10^{-3}$ s$^{-1}$. Hence although the neutral ligands show a $10^5$ advantage for 5-methyltetrazole, which has additional lone pairs to accommodate proton migration, for the anionic species the imidazolates are faster by 2–3 orders of magnitude. In comparison with the tautomerization of $H^+$ around the "imidazolate" ligand and that of $(NH_3)_5Co^{3+}$ a rate reduction of $1 \times 10^7$ is detected for the bulky group, but this path is still $2 \times 10^6$ faster than when both $(NH_3)_5Co^{3+}$ and $H^+$ must migrate in some concerted fashion.

**Driving Force of the Linkage Isomerization.** One is left with the question of the driving force of the Ad to R linkage isomerization. From the results using 5-methyltetrazolate as the ligand for $(NH_3)_5Co^{3+}$, the steric factor would favor isomer R thermodynamically. The influence of steric interaction may be estimated as about 3.0 kcal/mol.[3] The steric effect is also manifested in the direction of the linkage isomerization observed for the 4-methylimidazole complexes; thus, it is found that the R form is the thermodynamically favored product. The values of $\Delta H^\circ$ and $\Delta S^\circ$ found for the acid dissociation constants of R and Ad (eq 3) may be compared to the values for imidazole forming imidazolate ($\Delta H^\circ = 17.6 \pm 1.6$ kcal/mol, $\Delta S^\circ = -7 \pm 5$ eu)[32] and the values for $(CN)_5Fe(Him)^{2-}$ ($\Delta H^\circ = 8.8 \pm 0.8$ kcal/mol, $\Delta S^\circ = -21 \pm 3$ eu).[33] The acid dissociation constants of R and Ad are within 1 kcal for $\Delta H^\circ$ of the free ligand imidazole, suggesting an approximate cancellation of the withdrawing effect of Co(III) and the releasing effect of methyl on the ring. The more favorable $\Delta S^\circ$ for the dissociation of R and Ad vs. the neutral imidazole and anionic $(CN)_5Fe(imH)^{2-}$ complex would be anticipated on the basis of reducing positive charge on the Co(III) complex, separating opposite charges for the neutral organic molecule, and increasing charge separation for the anionic Fe(III) system. The solvation appears to be slightly different for the R, R$_{-H}$ and Ad, Ad$_{-H}$ pairs as shown by the 10-eu larger $\Delta S^\circ$ for dissociation of Ad, that is to say, a greater difference in solvation accompanies the deprotonation of Ad than for R. It seems logical for a pictorial view of the R and Ad isomers that the methyl group of R would perturb the solvation cage more than for the Ad isomer in the vicinity of the pyrrole hydrogen. A larger percentage change in solvation may then occur for the deprotonation of the Ad isomer upon establishing a strong H bond to the imidazolate anion, which is diminished if methyl perturbs the region.

A net lower free energy would exist for forming isomer R at the expense of Ad. That one is able to prepare isomer Ad must then be related to the kinetically slow linkage isomerization relative to the kinetic split between trapping either the R or the Ad orientation of 4-methylimidazole during the substitution process. R is the major product of the synthetic conditions. The entering ligand displaces $Me_2SO$ in the synthetic procedure. The orientation and the degree of solvation of the entering ligand or the products are likely to be quite different in $Me_2SO$ vs. those in $H_2O$, allowing formation of some Ad. It might also be mentioned that Toma[30] has concluded that histidine first coordinates to $(CN)_5Fe^{3-}$ in the hindered fashion, followed by rearrangement to the unstrained N. The isomerization at the $(CN)_5Fe^{3-}$ center is much more rapid than for $(NH_3)_5Co^{3+}$, which is entirely consistent with stronger Co$^{III}$–N bonds relative to Fe$^{II}$–N bonds and the magnitudes of the ligand field 10*Dq* values of related complexes.

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**Registry No.** $V \cdot 3Cl^-$ (A = $NH_3$), 86568-75-4; $VI \cdot 3Cl^-$ (A = $NH_3$), 86568-74-3; $(NH_3)_5Co(4\text{-methylimidazolate})^{2+} \cdot 2Cl^-$ (adjacent), 86568-76-5; $(NH_3)_5Co(4\text{-methylimidazolate})^{2+} \cdot 2Cl^-$ (remote), 86568-77-6; 4-methylimidazole, 822-36-6; $(NH_3)_5Co(\text{imidazole})^{3+} \cdot 3Cl^-$, 86630-87-7; $(NH_3)_5Co(2\text{-methylimidazole})^{3+} \cdot 3Cl^-$, 86568-78-7.

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# Beryllium Nitrogen Compounds. 1. Monomeric Bis(amido)beryllium Compounds

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Monomeric beryllium amides of type $Be(NR_2)_2$ were prepared, in part, by a new method. Bulky R groups prevent oligomerization. Bis(diisopropylamido)beryllium dimerizes slowly and also adds pyridine. Dicoordination of beryllium results in a high-frequency shift of the $^9Be$ NMR signal and a rather large line width relative to tricoordinate Be.

## Introduction

Among the amides of group 2A, those of the element beryllium are comparatively well characterized.[1] However, their chemistry is virtually unexplored. Four types of compounds are known, represented by the general formulas $Be(NR_2)_2$, $Be(N{=}CR_2)_2$, $XBeNR_2$ (X = organyl, hydride, halide), and $Be(NH_2)_3^-$. With the exception of $Be[N(SiMe_3)_2]_2$,[2] all beryllium bis(dialkylamides) do not exist as monomers. They dimerize, trimerize, or form adducts with Lewis bases such as pyridine to achieve tetracoordination at the beryllium center. BeN $\pi$-bonding, possible in BeN compounds of di- and tricoordinate Be, is obviously weak, and this is supported by data

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derived from vibrational spectroscopy[2,3] and bond lengths.[4]

Considering the remarkable BN bond strength observed in bis(amido)boron cations, $B(NR_2)_2^+$,[5,6] a comparative situation is to be expected for monomeric beryllium amides, $Be(NR_2)_2$, which are isoelectronic with these boron cations. However, only the above mentioned silyl species is known at the present time. Its BeN bond length (156.2 (24) pm)[4b] is quite long, indicating only weak BeN $\pi$-bonding. This may, however, also be due to SiN $\pi$-interaction. Therefore, it seemed desirable to extend the series of monomeric beryllium amides in order to obtain information on this point as well as on the steric factors preventing oligomerization.

## Experimental Section

The hydrolytic instability of beryllium amides required rigorous exclusion of moisture. No experimental difficulties were encountered by using the Schlenk-tube technique and dry, oxygen-free nitrogen gas. Solvents were distilled directly into the reaction vessels and solutions transferred by syringes.

$BeCl_2$ solutions in diethyl ether were prepared from Be powder and HCl in ether.[7] Solutions of organolithium compounds were commercial products (Hans Heinrich Hütte, Langelsheim) and were used after standardization as delivered. All amines were of commercial reagent grade. They were dried by $CaH_2$ and distilled prior to use.

The reactions were monitored by NMR spectroscopy ($^1H$, $^9Be$) using either a Bruker WP 200 or JEOL FX 90 multinuclei instrument. IR spectra were recorded with a Beckman 325 IR spectrometer. A Varian CH7 instrument was available for mass spectrometry. Elemental analyses were performed in the institute's analytical laboratory. Cryoscopy in cyclohexane was used for determining molecular masses. All precautions were taken to ensure safe working conditions and to avoid Be poisoning.

**Bis(bis(trimethylsilyl)amido)beryllium (1)** was prepared by the method of Bürger, Forker, and Goubeau:[2] yield 65%; bp 102 °C ($10^{-3}$ torr); mp −5 °C. Anal. Calcd for $C_{12}H_{36}BeN_2Si_4$: C, 43.69; H, 11.02. Found: C, 42.89; H, 11.00.

**Bis(diisopropylamido)beryllium (2).** A 100-mL two-necked flask equipped with reflux condenser, dropping funnel, and magnetic stirring bar was charged with 2.01 g (25 mmol) of anhydrous $BeCl_2$. A 6.9-mL quantity (50 mmol) of diisopropylamine was then added, and the mixture kept at reflux with stirring for 1 h. A grayish solid homogeneous mass had formed after cooling to ambient temperature. This mass was suspended in 20-mL of *n*-hexane. With continuous vigorous stirring, 32.1 mL of a 1.56 M solution of LiBu was added dropwise over a period of 30 min. The grayish suspension turned white, and the heat of the reaction caused reflux, which was continued for 3 h after the addition of LiR was complete. The insoluble material (0.73 g) was removed by filtration through a sintered-glass dish (G 3) and hexane removed from the filtrate in vacuo. A dark brown oil remained, which, on distillation, yielded 3.77 g (72%) of $Be(N\text{-}i\text{-}Pr_2)_2$: bp 78 °C ($10^{-2}$ torr); mp −15 °C. Anal. Calcd for $C_{12}H_{28}BeN_2$: C, 68.84; H, 13.51; N, 13.38. Found: C, 67.29; H, 13.31; N, 13.26. $M_r$: calcd, 209.4; found, 206.

**Dimerization.** A 2-g sample of **2** solidified on standing for 2 weeks completely. The crystals were washed with cold pentane to remove monomer; mp 96–96.5 °C. Anal. Calcd for $C_{24}H_{56}Be_2N_4$: C, 68.84; H, 13.51; N, 13.38. Found: C, 67.0; H, 13.2; N, 13.2. $M_r$: calcd, 418.8; found, 412.

**Bis(piperidino)beryllium (5).**[8] By use of the procedure as described for **2**, 2.52 g of $BeCl_2$ (32 mmol), 6.3 mL of piperidine (64 mmol), and 41 mL of a 1.56 M LiBu solution yielded 3.05 g (55%) of $Be(NC_5H_{10})_2$: mp 144–145.5 °C; sublimation at $10^{-2}$ torr at 140 °C oil-bath temperature. Anal. Calcd for $C_{10}H_{20}BeN_2$: C, 67.74; H, 11.39; N, 15.80. Found: C, 66.85; H, 11.26; N, 14.80. $M_r$: calcd, 177.3; found, 526.

**Bis(2,2,4,4-tetramethylpiperidino)beryllium (3).** A 4.9-mL quantity of tetramethylpiperidine was dissolved in 15 mL of diethyl ether and 17.3 mL of a 1.56 M LiBu solution in hexane added dropwise under stirring. The mixture was then kept for 2 h under reflux until no more butane escaped. The resulting clear solution was reacted with 13 mL of an ether solution of $BeCl_2$ containing 13.5 mmol of $BeCl_2$. An exothermic reaction produced a white precipitate and caused boiling of the solvent. A 1.07-g sample of insoluble material had formed, and 2.93 g of **3** (75%) was isolated from the filtrate by fractional distillation: bp 106 °C ($10^{-3}$ torr); mp ~−10 °C (glass formation). Anal. Calcd for $C_{18}H_{36}BeN_2$: C, 74.68; H, 12.53; N, 9.68. Found: C, 72.08; H, 12.37; N, 9.33. $M_r$: calcd, 289.5; found, 285.

**Bis((trimethylsilyl)-*tert*-butylamido)beryllium (4).** By use of the same procedure as for **3**, 5.0 mL of (27 mmol) $HNSiMe_3\text{-}t\text{-}Bu$ was reacted with 17.3 mL of 1.56 M LiBu followed by 13 mL of a $BeCl_2$ solution in ether (13.5 mmol of $BeCl_2$). A 2.65-g sample of **4** (66%) was isolated; bp 112 °C ($10^{-3}$ torr). Anal. Calcd for $C_{14}H_{36}BeN_2Si_2$: C, 56.50; H, 12.19; N, 9.41. Found: C, 55.42; H, 12.00; N, 9.07. $M_r$: calcd, 297.6; found, 294.

**Beryllium Chloride–Diisopropylamine.** A 12.5-mL sample of diisopropylamine (90 mmol) was dissolved in 25 mL of diethyl ether, and 10 mL of an ether solution containing 4.5 mmol of $BeCl_2$ was added over a period of 15 min with stirring. A brownish, heavy, oily layer was formed in a slightly exothermic reaction. No crystals separated from this oil in a refrigerator. Therefore, ether and excess amine were removed in vacuo. A solid off-white to grey-brown in color remained. Its weight became constant after 12 h at 35°C ($10^{-1}$ torr). The product decomposes at 80 °C without melting. Anal. Calcd for $C_6H_{15}BeCl_2N$: Cl, 39.15; N, 7.73. Found: Cl, 39.45; N, 7.88.

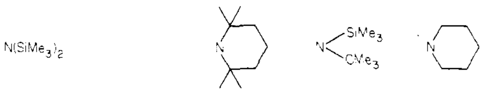
## Results and Discussion

Bis(amido)beryllium compounds can be conveniently prepared according to eq 1[9] and 2. Reactions following eq 1 are

$$2LiNR_2 + BeCl_2{\cdot}2OEt_2 \rightarrow Be(NR_2)_2 + 2LiCl + 2OEt_2 \quad (1)$$

$$2LiR + BeCl_2{\cdot}HNR_2 + HNR_2 \rightarrow Be(NR_2)_2 + 2LiCl + 2RH \quad (2)$$

$NR_2$



1 2 3 4 5

used advantageously if the lithium amide is soluble in the solvent used, thus providing homogeneous reaction conditions.[10] In contrast, reactions according to eq 2 are heterogeneous and limited to systems in which $BeCl_2$ forms amine complexes of type $BeCl_2{\cdot}D$. This is the case for D = diisopropylamine but not for D = 2,2,6,6-tetramethylpiperidine (Htmp) or hexamethyldisilazane.

Transamination reactions as described by eq 3 using mo-

$$Be(NR'_2)_2 + 2HNR_2 \rightarrow Be(NH_2)_2 + 2HNR'_2 \quad (3)$$

nomeric bis(2,2,4,4-tetramethylpiperidino)beryllium, $Be(tmp)_2$, and $HNMe_2$, or $Be(N\text{-}i\text{-}Pr_2)_2$ and $HNMe_2$, or Htmp and $HNC_5H_{10}$ were unsuccessful at temperatures up to the boiling point of the amine. Also, $Be[N(SiMe_3)_2]_2$ did not readily react with isopropylamine at reflux, but some SiN cleavage occurred according to the NMR data.[11]

Molecular mass studies of the beryllium amides **1–4** in cyclohexane prove the monomeric nature of these compounds

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(9) This method has been used previously,[2] but generally the aminolysis of diorganylberyllium compounds or organylberyllium hydrides was used for preparing $Be(NR_2)_2$ or $R'BeNR_2$ compounds.[1]

(10) A suspension of anhydrous finely ground $BeCl_2$ did not react with either $NaN(SiMe_3)_2$ or Li(tmp) in toluene under reflux conditions.

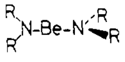
(11) Further studies are in progress to characterize intermediates and products.

Table I. NMR Data of the Bis(amido)beryllium Compounds **1-5** and Dimeric **2**[a]

| | 1 | 2 | 3 | 4 | $[2]_2$ | $[5]_3$ |
|---|---|---|---|---|---|---|
| $\delta(^9Be)$ ($h_{1/2}$) | 12.5 (180) | 12.7 (288) | 15.3 (230) | 15.1 (260) | 9.4 (106) | 9.24 (174); 1.09 (72) |
| $\delta(^1H)$ ($J$) | 0.19 | 1.095 d, $CH_3$ (6.35); 2.92, CH (6.35) | 1.28, $CH_3$; 1.45-1.75 m | 0.22, $SiCH_3$; 1.32, $CCH_3$ (1:1) | 1.405 d (6.59); 1.57 d (7.08); 3.38 s (6.59); 4.00 s (7.08) | 1.58; 2.80 sh; 3.09 |
| $\delta(^{13}C)$ | 3.98<br>117.8[b] | 26.10, $CH_3$ (95.7); 47.33, CH (103.4) | 19.07, C3 (140, t); 34.31, C6, C7 (120, q); 39.78, C2, C4 (125, t); 50.33, C1, C5 | 4.30, $SiCH_3$, (117.8); 35.60, $C\mathit{C}H_3$ (123, q); 51.67, $\mathit{C}CH_3$ | 24.03, C1[c] (73.25, q); 28.36, C3 (70.80, q); 47.59, C2 (35.36, d); 49,01, C4 (34.69, d) | 25.82<br>27.60<br>47.81 |
| $\delta(^{14}N)$ | −323 | −280 | | | | |

[a] All spectra were recorded in $C_6D_6$ solution (d = doublet, s = singlet, t = triplet, q = quartet, m = multiplet, sh = shoulder), and δ values refer to $SiMe_4$ as a standard for $^1H$ and $^{13}C$, a 1 M $BeCl_2$ solution for $^9Be$, and a saturated aqueous $NaNO_3$ solution for $^{14}N$ (δ in ppm; $J$ and half-widths in Hz). [b] $J(SiC)$ = 119 Hz. [c] C1 = $CH_3$ carbon of tricoordinate *i*-$Pr_2N$ group; C2 = CH carbon of the same group; C3 = $CH_3$ carbon of tetracoordinated *i*-$Pr_2N$ groups; C4 = CH carbon of the same group.

in solution. In contrast, bis(piperidino)beryllium (**5**) is trimeric. This is direct evidence that di- or trimerization of bis(dialkylamido)beryllium compounds is prevented by steric rather than electronic effects. Further support for this conclusion comes from the behavior of bis(diisopropylamido)beryllium (**2**). This compound, a clear, distillable liquid, crystallizes slowly at room temperature, and the crystals obtained were shown to be its dimer. Dimeric beryllium amides of type $Be(NR_2)_2$ have not yet been reported, but some of type $RBeNR'_2$ (R = Et, R′ = Me; R = Et, R′ = Ph) are described as dimeric. We therefore assign structures I–III for monomeric, dimeric, and trimeric bis(diorganylamido)beryllium compounds. Structure III was established for $[Be(NMe_2)_2]_3$, as ascertained by X-ray crystallography.[4c] The allene-type structure I was determined for **1** in the gas phase,[4b] and NMR data of the compounds described in this work are in accord with these constitutions.



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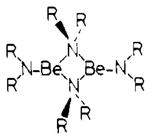

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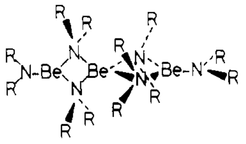

III

The NMR data observed for monomeric **1–4**, dimeric **2**, and trimeric **5** are summarized in Table I. As observed previously,[2] **1** exhibits only a single proton signal, indicating that all 36 protons are magnetically equivalent. Similarly, two $^1H$ NMR signals are observed for **4**, each representing the protons for the $SiMe_3$ and $CMe_3$ group.

The $^1H$ NMR signals for **1–4** are all found at higher frequencies as compared to those of the free base. This corresponds to trends found in a series of aminoboranes and reflects both the change in hybridization at nitrogen as well as possible electron withdrawal due to BeN π-bonding. An even larger low-field shift is observed for protons in bridging $R_2N$ groups, a result of the formal positive charge at tetracoordinate nitrogen. This affects even the terminal $R_2N$ groups bound to tricoordinate Be more strongly than the $R_2N$ groups in dicoordinate beryllium compounds. While chemical shifts, multiplicity, intensities, and coupling constants of the data obtained correspond fully with expectations for structures I and II, only three $^{13}C$ resonances and three rather broad $^1H$ resonances are observed for trimeric **5**. Therefore, exchange of the piperidino groups in the NMR time scale is indicated—in contrast to the case of dimeric **2**. However, two distinct, though rather broad, signals for tetracoordinate ($\delta(^9Be)$ 1.09) and tricoordinate ($\delta(^9Be)$ 9.24) beryllium in a 2:1 ratio are observed for **5**. Therefore, amine group exchange must be faster than beryllium exchange.

It is well-known that the coordination number for beryllium has a significant effect on both chemical shift and line width.[12] While the δ range for tetracoordinate beryllium is rather small, depending on the electronegativity of the substituents,[13] only few $\delta(^9Be)$ values for tricoordinate beryllium have so far been reported ($[Be(O\text{-}t\text{-}Bu)_2]_3$ and $[Be(NMe_2)_2]_3$).[11,14] The signals for Be with coordination number 3 are found on the low-frequency side of tetracoordinated beryllium species, and the data for dimeric **2** and trimeric **5** provide additional examples. $\delta(^9Be)$ data for two-coordinate beryllium have not yet been reported. As expected, the chemical shifts indicate strong deshielding at the Be nucleus. This is not at all unusual considering the similar trend in $\delta(^{11}B)$ values for comparable BN compounds with coordination numbers 4–2.[15] The coordination number of beryllium is therefore easily detected by $^9Be$ NMR spectroscopy.

The line width of the $^9Be$ signals increases as the coordination number decreases. This is to be expected for quadrupolar effects and reduced symmetry and hence larger field gradients at the beryllium nucleus. In our case, rapid relaxation is also favored because the atoms next to beryllium are $^{14}N$ atoms having also a quadrupolar nucleus.

Substitution of H in an amine $HNR_2$ by beryllium induces a shift of the $^{14}N$ NMR signal to higher frequency. The shift difference $\Delta(^{14}N)$ for **1** is 18 and for **2** 28 ppm. These shifts are rather similar to those observed for aminoboranes.[16] Although only two data are presently available for the beryllium amides, it appears that $\Delta(^{14}N)$ values are larger in the boron series, which would be in accord with a rather more polar Be–N bond containing less π-character than the corresponding B–N bond.

While NMR data of the new monomeric beryllium bis(amides) are unequivocal, it is difficult to assign definitely $\nu(BeN_2)$ from IR data alone.[17] According to Bürger et al.,[2] the frequency for $\nu_{as}(BeN_2)$ was found at 1325 cm⁻¹ and for $\nu_s(BeN_2)$ at 400 cm⁻¹ in the Raman spectrum. This suggests a rather weak BeN bond as compared to the BN bond in

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$R_2NBNR_2^+$ ($\nu_{as}(BN_2)$ 1956 $\text{cm}^{-1}$[6]). In most cases, we observe a fairly strong band in the 1200–1300-$\text{cm}^{-1}$ region, which we believe to be associated with $\nu_{as}(BeN_2)$.

Mass spectra of **1**–**4**, taken at 15 and 70 eV, show no general pattern. Surprisingly, the intensity of the molecular ion was weak in all cases, an (M − 15) peak usually being the base peak. Only $M^+$ of **3** had a fairly high intensity (11% at 70 eV). The beryllium atom is readily removed in the fragmentation process by breaking the BeN bond with formation of $R_2N^+$, $R_2NH^+$, and $SiMe_3^+$ and further fragmentation of these species. Again, **3** provides an exception, insofar, as fragments in the ranges *m/e* 274–276, 258–260, and 149–151 contain Be, as shown by good agreement between observed and calculated peak patterns. Interestingly, $M^+$ of dimeric **2** is quite intense (25%), and the molecular ion decomposes in two ways: (i) by fragmentation into $M^+$ of monomeric **2**, ascertained by a metastable peak, and (ii) by cleavage of one BeN bond, leading to a fragment of *m/e* 318. The base peak in this case is $(M - 15)^+$ of monomeric **2**.

## Chemical Behavior

**1**–**4** are quite susceptible to hydrolysis with formation of $Be(OH)_2$ and the amine. They are, however, stable toward oxygen at room temperature.

The compounds can be readily mixed with ether, tetrahydrofuran, monoglyme, and diglyme, and $^9$Be NMR shows that these ethers will not coordinate. Also, **1**–**4** dissolve in hexane, cyclohexane, benzene, and toluene. Again, neither $\delta(^9\text{Be})$ nor the line width is affected.

In contrast, **2** reacts with pyridine only, forming a deep red solution in benzene or cyclohexane. Although we have been unable to isolate an analytically pure adduct, NMR data provide strong evidence for a 1:1 adduct: the $^9$Be signal is shifted to 11.5 ppm, $h_{1/2}$ = 155 Hz, data typical for tricoordinate beryllium. Both data remain virtually unaffected on adding more pyridine, and the same holds for the $^1$H NMR spectrum ($\delta(^1\text{H})$ 1.10 doublet, 3.40 septet, 6.68, 7.04, 8.50). The signals for pyridine are somewhat broad and are further broadened on adding pyridine, thus indicating pyridine exchange at the recording temperature. This result indicates that monomeric beryllium bis(amides) are weak Lewis acids and electrophiles. They are generally not susceptible to transamination with secondary amines due to steric hindrance. However, the action of pyridine on **2** suggests that less bulky amines such as primary amines and ammonia will interact, especially with **2**, the least sterically hindered monomeric $Be(NR_2)_2$, and some preliminary data support this expectation.[17]

## Conclusion

There is obviously a close relationship between the existence of monomer bis(alkylamido)beryllium compounds and bis(dialkylamido)boron cations because each of the beryllium amides **1**–**4** reported here has an isoelectronic and isotructural counterpart $(R_2N)_2B^+$ ($R_2N$ = N-*i*-$Pr_2$;[5] tmp, $NEt_2$,[6] N-$(SiMe_3)_2$;[18] $NCMe_3SiMe_3$[18]). It will, therefore, be interesting to see whether it is possible to also prepare and investigate monomeric beryllium amides of type $RBeNR_2$, formally possessing an electron sextet structure in analogy to $R'BNR_2^+$.[6] Some of these boron cations with bulky R′ groups are stable in solution for a short while even at room temperature.[18]

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[18] H. Nöth and S. Weber, unpublished work, 1982.

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# Pentacyanoferrate(II) Complexes of Pyrimidine and Quinoxaline

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The ions pentacyano(pyrimidine)ferrate(II) and pentacyano(quinoxaline)ferrate(II) have been characterized in aqueous solution. The complexes exhibit strong metal-to-ligand charge-transfer absorptions respectively at 410 nm ($\epsilon_{max} = 3.1 \times 10^3$ $M^{-1}$ $cm^{-1}$) and 545 nm ($6.0 \times 10^3$ $M^{-1}$ $cm^{-1}$). In the presence of excess heterocycle, the rate law for formation of the complexes from pentacyanoaquaferrate(II) ion is $d[Fe(CN)_5L^{2-}]/dt = k_f[Fe(CN)_5OH_2^{3-}][L]$. For the pyrimidine reaction, $k_f = 340 \pm 25$ $M^{-1}$ $s^{-1}$ (25 °C, 0.10 M ($LiClO_4$)), $\Delta H^* = 15.5 \pm 1$ kcal $mol^{-1}$, and $\Delta S^* = 6 \pm 3$ cal $mol^{-1}$ $deg^{-1}$. In the quinoxaline case, $k_f = 425 \pm 25$ $M^{-1}$ $s^{-1}$, $\Delta H^* = 15.2 \pm 1$ kcal $mol^{-1}$, and $\Delta S^* = 6 \pm 3$ cal $mol^{-1}$ $deg^{-1}$. Ligand-exchange studies yielded values for the specific rates of dissociation. For the pyrimidine complex, $k_d = (1.3 \pm 0.1) \times 10^{-3}$ $s^{-1}$, $\Delta H^* = 21.8 \pm 2$ kcal $mol^{-1}$, and $\Delta S^* = 2 \pm 6$ cal $mol^{-1}$ $deg^{-1}$. For quinoxaline, $k_d = 0.62 \pm 0.10$ $s^{-1}$, $\Delta H^* = 19.6 \pm 2$ kcal $mol^{-1}$, and $\Delta S^* = 4 \pm 6$ cal $deg^{-1}$ $mol^{-1}$. One-electron oxidation of the complexes by cyclic voltammetry is reversible, with $E_f = -0.52$ and $-0.55 \pm 0.03$ V vs. NHE, respectively, for the pyrimidine and quinoxaline complexes. The stabilities of the iron(III) complexes can be estimated from the electrochemical results and ligand substitution properties of the iron(II) species.

## Introduction

The chemistry of substituted pentacyanoferrate(II) complexes, $Fe(CN)_5L^{3-}$, where L represents an aromatic N-heterocycle, saturated amine, or other donor ligand, has proved to be a rich source of information about metal–ligand interactions. Initially undertaken to probe for d$\pi$–p$\pi$ back-bonding between Fe(II) and various ligand systems, studies of $Fe(CN)_5L^{3-}$ species have produced a number of new complex ions whose spectra and photochemical and electrochemical properties are of significance and utility.[2-16]

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