140 *Inorg. Chem.* **1990**, *29*, 140-143

extinction coefficient[11] for [Co(aben)Cl(py)] is independent of pressure, the concentration of the five-coordinate species [Co(aben)Cl] is found to be 7.7% at atmospheric pressure, being larger than the previous value of 4%.[3c] Moreover, the thermodynamic parameters for the equilibrium (1) are calculated with [py] = 12.41 M as follows: $K = 0.96\ \mathrm{M}^{-1}$, $\Delta G = 0.099\ \mathrm{kJ\ mol}^{-1}$, and $\Delta S = -0.18\ \mathrm{kJ\ mol}^{-1}\ \mathrm{K}^{-1}$.

Acknowledgment. We thank Y. Yoshida for technical assistance. This work was supported in part by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture of Japan (No. 59470038).

Registry No. py, 110-86-1; [Co(aben)Cl], 36433-98-4.

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[11] The molar extinction coefficients are estimated to be 4290 $\mathrm{M}^{-1}\ \mathrm{cm}^{-1}$ at 21 500 cm^{-1} for [Co(aben)Cl(py)] and 3450 $\mathrm{M}^{-1}\ \mathrm{cm}^{-1}$ at 12 300 cm^{-1} for [Co(aben)Cl].

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Amination of Coordinated Nitriles: Synthesis of Metal Complexes of Amidines and Guanidines

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Coordination by nitriles to electron-withdrawing metal ions results in considerable enhancement in the electrophilicity of the nitrile carbon center. This is demonstrated[1] by the 10^6–10^8-fold increase in the rate of base-catalyzed hydration of nitriles when bound to $(NH_3)_5M^{3+}$ (M = Co(III), Rh(III), Ru(III)), although metal ions such as Ru(II) (which are strongly metal-to-ligand π-bonding) have little influence on this reactivity.[1] The susceptibility of coordinated nitriles to attack by other nucleophiles (e.g. CN^-, N_3^-, and CO_3^{2-})[2-5] prompted the present work, where we have used liquid NH_3 to aminate nitriles, including a substituted cyanamide, providing a synthesis of metal complexes of unidentate amidines and of a (substituted) guanidine. We were particularly interested in comparing the acid/base properties and solution structures of such complexes with those of their isoelectronic N- and O-bonded urea and amide complexes.[6] This study may be relevant to the in vivo coordination chemistry of arginine residues, which contain protonated guanidine derivatives as potential ligands for bio-constituent metal ions.

Results and Discussion

The series of yellow nitrile complexes $[(NH_3)_5Co\text{-}NCR]^{3+}$ (R = NH_2, $N(CH_3)_2$, CH_3, $CH_2{=}CH$, C_6H_5, $o\text{-}NO_2\text{-}C_6H_4$, $p\text{-}F\text{-}C_6H_4$) were prepared by the reaction of $[(NH_3)_5CoOSO_2CF_3](CF_3SO_3)_2$ with the appropriate nitrile, either as the neat compound or in acetone.[2,7] When dissolved in NH_3(l), they undergo a slow reaction (minutes at −76 °C), evidenced by the distinct color change from yellow to burgundy (R = $N(CH_3)_2$) or yellow-orange; the R = NH_2 derivative merely deprotonates at the exo NH_2 and does not aminate. The solvent was evaporated, giving quantitative yields of amination products, which were recrystallized (water) and characterized by microanalyses and NMR (^{1}H, ^{13}C) and absorption spectra.

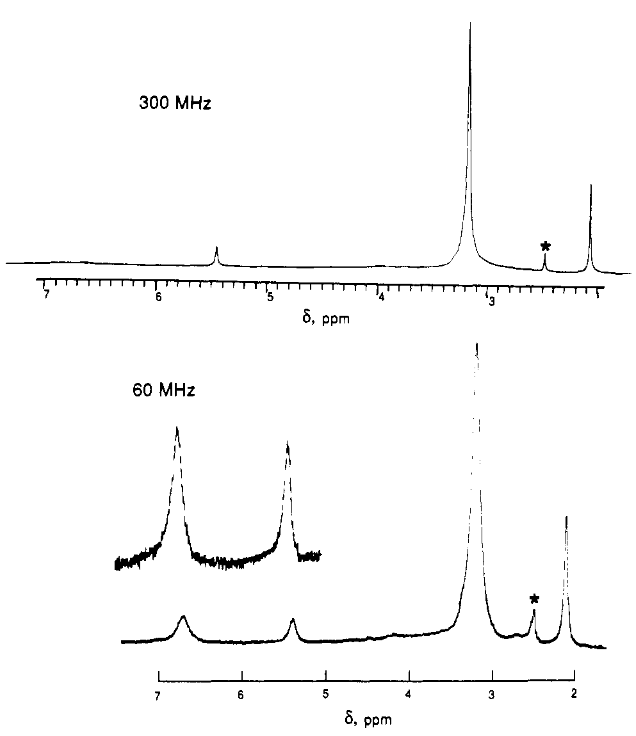

Figure 1. 60-MHz (35 °C, bottom) and 300-MHz (20 °C, top) ^{1}H NMR spectra of $[(NH_3)_5CoNH{=}C(NH_2)CH_3]^{3+}$ in Me_2SO showing the collapse of the exo-NH_2 signal at the higher field strength. These spectra were run with the same sample but are not on the same scale; the asterisk represents residual $Me_2SO\text{-}d_5$ in the solvent.

Amidines. The aqueous recrystallization of products obtained from either alkyl or aryl nitrile complexes in NH_3, with use of either Tris/$NaClO_4$ (pH ca. 9) or $HClO_4$, gave yellow-orange crystals with identical properties (for a particular nitrile). Each material gave the correct analysis for addition of 1 mol of NH_3, $[(NH_3)_5CoNCRNH_3](ClO_4)_3\cdot xH_2O$, and the cation-exchange behavior (Sephadex C25 resin) indicated a 3+ ion. The 60-MHz ^{1}H NMR spectrum of the prototype $[(NH_3)_5Co{-}NH{=}C(NH_2)CH_3]^{3+}$ in $Me_2SO\text{-}d_6$ (Figure 1, bottom) shows coincident cis- and trans-NH_3 signals (δ 3.26 ppm, 15 H), not uncommon for CoN_6 species,[6] lattice water (δ 3.42 ppm, 4 H), the methyl signal (δ 2.12 ppm, 3 H), and broad signals at δ 6.68 (2 H) and 5.39 (1 H) ppm, typical[8] of imine (NH=C) protons. None of these signals corresponds to residual free NH_3 or NH_4^+ or unreacted nitrile complex (δ 3.70 ppm, cis NH_3; δ 3.33 ppm, trans NH_3; δ 2.60 ppm, CH_3). These data allow formulation of the product as $[(NH_3)_5Co{-}NH{=}C(NH_2)CH_3](ClO_4)_3\cdot 2H_2O$, and similar considerations apply to the other amidine complexes (Table I). The ^{13}C NMR data confirmed the presence of the amidine ligands and the purity of the complexes (Table II).

These results indicate that at least up to pH 10 the amidine ligands are uncharged, and the complexes are stable in neutral or acid solution for many hours, although slow aquation (amidine release) ultimately occurs ($t_{1/2} > 10$ h). There seems to be no hydrolysis of the ligand to produce (initially) the N-bonded amide, $[(NH_3)_5CoNH{=}C(OH)R]^{2+}$. Above ca. pH 11, deprotonation can be observed spectrophotometrically, and indeed brown-orange deprotonated forms can be readily crystallized from 0.1 M OH^- (although prolonged exposure to strong base (1 M) results in decomposition). These revert to the protonated amidine species

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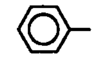
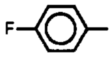
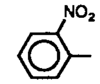
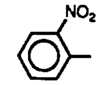
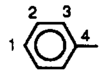
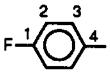
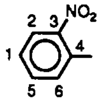
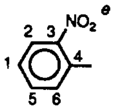
Table I. Proton NMR Spectral Data for the Amidine and Guanidine Derivatives $[(NH_3)_5Co—NH_mC(NH_n)R]^{l+}$ in Me_2SO-d_6

R	δ, ppm^a cis NH_3	trans NH_3	NH_m	NH_n^{b,c}	other^{b,c}	assignt
			Protonated Species^d			
$-CH_3$	3.26	3.26	5.48	ca. 6.8 (2) br	3.42 (2)	H_2O^h
					2.15 (3)	CH_3
			5.39^i	6.68 (2)^i	2.12 (3)^i	CH_3^{i}
					3.36 (2)	H_2O^h
	3.38	3.29	5.77	7.30 (2) br	7.57–7.66 (5) m	phenyl
	3.37	3.28	5.77	7.30 (2) br	7.41–7.69 (5) m	phenyl
	3.36	3.36	6.23	7.58 (2) br	7.78–8.3 (5) m	phenyl
			Deprotonated Species^e			
$-CH_3$^{e}	3.29	3.18	*g*	*g*	2.06 (3)	CH_3
	3.47	3.15	*g*	5.32	7.52–8.00 (5) m	phenyl
$-N(CH_3)_2$^{f}	3.31	3.12		5.67 (2)	2.94	N-CH_3
					3.40	H_2O^h

^{a}Shifts downfield from the internal reference TMS. ^{b}The number of protons is given in parentheses. ^{c}br = very broad; m = multiplet. ^{d}$l = 3$, $m = 1$, $n = 2$. ^{e}$l = 2$, $m = 1$, $n = 1$. ^{f}$l = 2$, $m = 0$, $n = 2$. ^{g}Not observed (see text). ^{h}Lattice water. ^{i}60-MHz spectrum at 35 °C; all others 300 MHz at 20 °C.

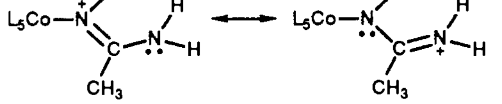
Table II. Carbon-13 NMR Spectral Data for the Amidine and Guanidine Derivatives $[(NH_3)_5Co$-$NH_mC(NH_n)R]^{l+}$ in Me_2SO-d_6 at 20 °C

R	δ, ppm^a N⋯C⋯N	other^{c,d}	assignt
	Protonated Species^b		
$-CH_3$	105.49	−42.25	CH_3
	105.64	68.81	1
		65.23	4
		62.15 (2)	
		60.86 (2)	
	104.54	97.44 d [250]	1
		65.26 d [3]	4
		63.56 (2) d [9]	3
		49.10 (2) d [22]	2
	103.25	78.52	3
		68.46	1
		65.50	2
		64.86	6
		58.38	4, 5
		57.21	
	Deprotonated Species		
$-CH_3$^{e}	105.61	−41.88	CH_3
	105.61	79.13	3
		67.89	1
		62.63	2, 4, 5, 6
		62.58	
		57.98	
		55.58	
$-N(CH_3)_2$^{f}	95.98	−27.77	N-CH_3

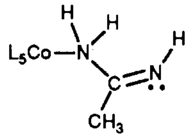
^{a}Shifts downfield from the internal reference dioxane (δ 66.26 ppm vs TMS). ^{b}$l = 3$, $m = 1$, $n = 2$. ^{c}The number of carbons in parentheses. ^{d}d = doublet; the C–F coupling constant *J* (in Hz) is given in brackets. ^{e}$l = 2$, $m = 1$, $n = 1$. ^{f}$l = 2$, $m = 0$, $n = 2$.

in acid, confirming the acid/base relationship. The eluted as 2+ ions on Sephadex resin with 0.1 M NaOH as eluant, and the only analyzed derivative corresponded to the expected $[(NH_3)_5CoNH{=}C(NH)CH_3](ClO_4)_2$ (amidine proton positions inferred—see below).

For complexes of both uncharged and deprotonated amidine there are alternative tautomeric forms. The spectrum shown in Figure 1 (bottom) is consistent with either of the formulations $[(NH_3)_5CoNH{=}C(NH_2)CH_3]^{3+}$ or $[(NH_3)_5CoNH_2C({=}NH)CH_3]^{3+}$. The distinction between these tautomers rests with, among other things, the inequivalence of the NH protons. All the imine protons for species **1** are inequivalent, if **1b** contributes,



1a **1b**



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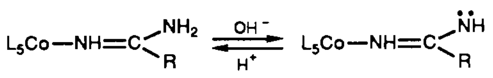
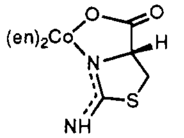
and rapid rotation about the exo-C⋯NH_2 bond needs to be invoked to accommodate their observed equivalence in the 60-MHz ^1H NMR spectrum. For species **2**, protonation at the Co-bonded N has prevented resonance, and the Co—NH_2 protons are equivalent. The issue was resolved by observation at higher field strength (300 MHz) and lower temperature (20 °C), where the NH_2 signal is at the point of collapse into the base line while the other NH proton resonance remains unaffected (Figure 1, top). This result confirms the proton inequivalence and hence structure **1** for the protonated amidine complex (with a nontrivial contribution from **1b** but, as argued ahead, not a large contribution). The other amidines behaved similarly (Table I), and these solution structures are consistent with solid-state structures of several chelated amidines (or thioamidine) known crystallography to contain the two protons on the exo-N atom.[8] The present amidine complexes are the first simple *unidentate* cobalt(III) complexes of this kind.

Although the crystalline solids $[(NH_3)_5CoNH{=}C(NH_2)R](ClO_4)_3$ and $[(NH_3)_5CoNH{=}C(NH)R](CoO_4)_2$ are visually quite distinct, the visible absorption spectrum of $[(NH_3)_5CoNH{=}C(NH_2)CH_3]^{3+}$ (ϵ_{484} 77.5) did not change substantially on deprotonation in 0.1 M OH^- (ϵ_{485}, 83). This is consistent with the removal of a proton remote from the chromophore, without significant electron reorganization of the resultant ligand (as found with acid/base equilibria of N-bonded amides):[6]



Thus, the deprotonated amidines may be formulated as $[(NH_3)_5CoNH{=}C(NH)R]^{2+}$ rather than $[(NH_3)_5CoN{=}C(NH_2)CH_3]^{2+}$. Consistent with this formulation, the deprotonated complex $[(NH_3)_5CoNH{=}C(NH)(C_6H_4NO_2)]^{2+}$ showed a single amidine NH resonance that was integrated as one proton (δ 5.32); the other NH proton was not observed. The chemical shift for this proton was similar to that found (δ 5.33) for the exo-N center of the chelated amidine of known[8] structure (solid state)



For the $[(NH_3)_5CoNH{=}C(NH)CH_3]^{2+}$ complex, neither NH proton was observed. This can be understood if these protons on the basic N centers undergo (on the NMR time scale) exchange with trace water present in the Me_2SO solvent. Such a phenomenon has been observed previously for $[(NH_3)_5CoNC(NH)]^{2+}$, $[(NH_3)_5CoOH]^{2+}$, and $[(NH_3)_5CoNHSO_3]^{+}$, for example,[6] and each of the exchanging protons in these molecules is *less* basic than the exo NH of $[(NH_3)_5CoNH{=}C(NH)R]^{2+}$. We have even observed[6] selective exchange broadening of one of the two carboxamide NH protons ($pK_b \approx 3$!) of $[(NH_3)_5CoOC(NH_2)CH_3]^{3+}$ and $[(NH_3)_5CoOC(NH_2)H]^{3+}$, attributable to the presence of trace water.

Acidity arguments can be used to support the structural assignments of the amidine complexes. We have shown previously that a complex such as $[(NH_3)_5CoNH_2COR]^{3+}$ will exist in acid solution as its least acidic form.[6] Thus, for N-bonded amides, the preferred tautomer is $[(NH_3)_5CoNH{=}C(OH)R]^{3+}$ ($pK'_a \approx 3$), while for N-bonded ureas the structure is $[(NH_3)_5CoNH_2{-}CO{-}NR'R]^{3+}$ ($pK'_a \approx 3$).[2,6] These results indicate a pK'_a value of 3 *or less* for the structure $[(NH_3)_5CoNH_2COR]^{3+}$. Hence, if $[(NH_3)_5CoNH_2C({=}NH)R]^{3+}$ is considered isoelectronic with $[(NH_3)_5CoNH_2C({=}O)R]^{3+}$, then it might also be acidic ($pK'_a \leq 3$). Since the observed $pK'_a > 10$, the preferred structure is more likely $[(NH_3)_5CoNH{=}C(NH_2)R]^{3+}$, in agreement with the conclusion earlier. When we extend this analogy, the assignment is also in accord with known acidities[6] of $[(NH_3)_5Co{-}OC(NH_2)R]^{3+}$ ($pK'_a \approx 11$), which are isoelectronic with $[(NH_3)_5CoNH{=}C(NH_2)R]^{3+}$.

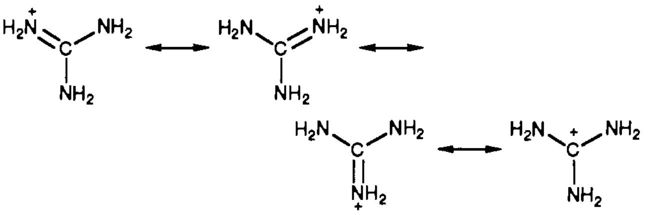
The acetamidinium ion has a reported[9] pK'_a value of 12.4, acetamidine itself probably has $pK'_a \gg 16$, and its Co(III) complex has a pK'_a value of ca. 11. This enhancement ($\geq 10^5$) in acidity on coordination to Co(III) is usual, although the magnitude is usually less than for binding to H^+. Enhancements for organic molecules bonded to $(NH_3)_5Co^{III}$ range enormously, from about 10 to about 10^{13}.[10]

Substituted Guanidine. The unsubstituted cyanamide complex[11] $[(NH_3)_5CoNCNH_2]^{3+}$ instantly deprotonates in liquid NH_3 to yield the unreactive ion $[(NH_3)_5CoNCNH]^{2+}$; this is similar to the situation in aqueous base.[11] However *N*,*N*-dimethyl substitution eliminates the possibility of deprotonation, and $[(NH_3)_5CoNCN(CH_3)_2](CF_3SO_3)_3$[2] quickly (but not instantaneously) changes color from yellow to deep burgundy in liquid NH_3, indicative of amination to yield the deprotonated substituted-guanidine species "$[(NH_3)_5CoNH{=}C(NH)N(CH_3)_2]^{2+}$". Evaporation of the ammonia left a deposit of gleaming burgundy crystals of the ditriflate salt. This deprotonated form was obtained from basic, neutral, and even acid solution as both the ditriflate and diperchlorate salts. It is very stable in Me_2SO, H_2O, or dilute base, but in strong acid the ligand is rapidly lost (vide infra).

The low pK'_a value for $[(NH_3)_5CoNH{=}C(NH_2)N(CH_3)_2]^{3+}$ contrasts sharply with that of the amidines, where the corresponding $pK'_a \approx 11$. This is not the only difference. The ^1H NMR spectrum of the isolated deprotonated species "$[(NH_3)_5CoNH{=}C(NH)N(CH_3)_2]^{2+}$" exhibits the cis- and trans-NH_3 signals characteristic of an N-bonded pentaammine complex (Table I), but it shows only one NH signal in the imine region, which gives an integration for two protons and which is consistent with the alternative structure $[(NH_3)_5CoNC(NH_2)N(CH_3)_2]^{2+}$. Also, the visible spectrum shows ϵ_{511}(max) 102, consistent with the $Co{-}\ddot{N}{=}C$ arrangement as argued previously[6] and again contrasting with that of the deprotonated amidine $[(NH_3)_5CoNH{=}C(NH)CH_3]^{2+}$ (ϵ_{485}(max) 83).

In acid solution free dimethylguanidinium ion and $[(NH_3)_5CoOH_2]^{3+}$ arise from the hydrolysis of $[(NH_3)_5CoNH{=}C(NH_2)N(CH_3)_2]^{3+}$, at a rate linear in $[H^+]$ for a 2-fold variation in the range 0.12–0.24 M (μ = 1.0 M; $NaClO_4$); in 0.12 M $HClO_4$, k(obsd) = $(2.77 \pm 0.03) \times 10^{-2}$ s^{-1}, and in 0.24 M $HClO_4$, k(obsd) = $(6.01 \pm 0.24) \times 10^{-2}$ s^{-1}. Clearly the complex is not appreciably protonated in this pH region ($pK'_a \ll 1$), and the protonated form is obviously very reactive ($t_{1/2} \leq 1$ s). This reactivity contrasts sharply with the amidine chemistry.

Free dimethylguanidine, like the parent guanidine, is a very strong base in water: $pK'_b \approx 0.4$; i.e., the protonated forms are weak acids ($pK'_a \approx 13.6$).[11] The ability of the free base to *lose* a proton is unknown, but guanidine itself does not self-deprotonate to become zwitterionic and must therefore be an extremely weak acid ($pK'_a \gg 16$). However, on coordination to Co(III), the neutral ligand becomes a very strong acid ($pK'_a < 1$) and the enhancement in acidity is $\gg 10^{15}$! Large enhancements ($<10^{10}$) in acidity for ligands N-bonded to cobalt(III) such as ureas,[2] amides,[1,13] sulfamate,[14] sulfonamide,[15] cyanamides,[11] sulfinamides,[6] and carbamates[6,16] are known, but the enhancement here is possibly the greatest reported to date. Factors influencing the acidity of guanidine are not necessarily related to those determining its basicity. It is a good base because its protonated form is flat and is stabilized by π-conjugation:



The sensitivity of the acidity of amidinium and especially guanidinium ions to the nature of the electron-withdrawing substituents has been noted and discussed by Charton.[17] However, it is not clear that such substituents (CN^-, for example) would enhance the acidity of the neutral molecules similarly, although $(NH_3)_5Co$– certainly does for at least one guanidine derivative.

Platinum(II) complexes of substituted guanidines have been reported recently,[18] and the ligands were suggested to be in the uncharged rather than deprotonated form although ligand deprotonation and tautomerism were not considered. Platinum(II) complexes of amidines (not unidentate) have been reported,[19] and it was believed (but not proven) that the amidine arose by addition of amine to a coordinated nitrile. Also, C- and N-bonded N,-N'-substituted formamidine complexes of Co(III) have been described.[20]

Finally, the extreme reactivity of the protonated guanidine species $[(NH_3)_5Co{-}NH{=}C(NH_2)N(CH_3)_2]^{3+}$ ($t_{1/2} < 1$ s) is in

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keeping with the reactivities observed for other N-bonded complexes of this kind, $[(NH_3)_5CoNH_2SO_2NH_2]^{3+}$, $[(NH_3)_5CoNH_2SOCH_3]^{3+}$, $[(NH_3)_5CoNH_2CONR_2]^{3+}$, and $[(NH_3)_5CoNH_2CO(OC_2H_5)]^{3+}$, all of which have a very acidic proton ($pK'_a \leq 3$) on the nitrogen bound to Co.[6] The amidine complexes, on the other hand, are very much less reactive ($t_{1/2} > 10$ h) and less acidic. The apparent correlation between reactivity and acidity breaks down with complexes such as amide-*N* species, which, although quite acidic, are not very reactive.[6] However, we have argued that the protonated amidine and amide complexes are each of the Co—NH= kind, and all these results can be rationalized if the Co—NH$_2$R bond (electron-withdrawing R) is appreciably weaker than the Co—NH= bond and the reactions have an appreciable dissociative component.

Experimental Section

Electronic spectra were measured by Cary 210 and Cary 118C instruments, thermostated to 25.0 ± 0.1 °C by water circulation from Lauda baths. Details of our kinetic techniques and data analysis are described elsewhere.[2,6] The hydrolysis reactions were sufficiently slow to follow in situ in a cell thermostated within the spectrophotometer and were monitored at 520 nm by using 0.1–0.32 M $HClO_4$ at constant ionic strength (1.17 M; $NaClO_4$). Reported specific rates are the means of quadruplicate determinations. The chromatography (below) and final spectra were consistent with 100% $[(NH_3)_5CoOH_2]^{3+}$ as product (ϵ_{490} 47.7). NMR spectra were recorded on either Varian T60 (^{1}H; probe temperature 30 °C) or Varian XL-300 (^{13}C, ^{1}H; probe temperature 20 °C) instruments for Me_2SO-d_6 solutions using dioxane (^{13}C) or tetramethylsilane (^{1}H) as the internal references. Chemical shifts are reported as positive downfield from TMS (^{1}H) or dioxane (^{13}C). Chemicals were AnalaR grade or the equivalent. Cation-exchange chromatography was carried out with use of SP Sephadex C25 (Na^+ form) cation resin and 0.23 M Na^+ eluant (pH 7; 0.01 M $H_2PO_4^-$, 0.01 M HPO_4^{2-}, 0.2 M Cl^-). Salts of the nitrile complex ions $[(NH_3)_5CoNCR]^{3+}$ were obtained from $[(NH_3)_5CoOSO_2CF_3](CF_3SO_3)_2$[21] as perchlorate or trifluoromethanesulfonate salts as described elsewhere.[7]

$[(NH_3)_5CoNH{=}C(NH_2)R](ClO_4)_3$. $[(NH_3)_5CoNCR](ClO_4)_3$ (2.0 g) was dissolved in NH_3(l) (ca. 50 mL) in an open but narrow-necked flask. Within minutes the solution changed color from yellow to orange-yellow. The ammonia was allowed to evaporate and the treatment with NH_3(l) repeated. The residue was recrystallized from a minimum volume of water with use of either aqueous $NaClO_4$ or $HClO_4$ as precipitant. Samples contaminated with a small amount of $[(NH_3)_5CoOH_2](ClO_4)_3$ were recrystallized from water/$NaClO_4$ containing Tris (0.02 M), which kept the aqua complex in solution as its more soluble hydroxo form. Some of the products proved to be hydrates, as shown by ^{1}H NMR spectroscopy in dry Me_2SO, but lattice water was removed under vacuum over P_2O_5. Anal. Calcd for $[(NH_3)_5CoNH{=}C(NH_2)CH_3](ClO_4)_3$: C, 4.80; H, 4.20; N, 19.58; Cl, 21.28. Found: C, 4.60; H, 4.36; N, 19.30; Cl, 21.13. Visible spectrum: ϵ_{484}(max) 77.5 (0.01 M $HClO_4$).

$[(NH_3)_5CoNH{=}C(NH)R](ClO_4)_2$. Only the methyl and *o*-nitrophenyl derivatives were characterized. To a thin slurry of the protonated form in water was added 1 M NaOH dropwise until it just dissolved. (N.B. Too much OH^- can lead to decomposition.) The solution, which had darkened, was filtered and treated with a $^1/_5$ volume of saturated aqueous $NaClO_4$. Crystals deposited readily, and after they were cooled at 0 °C for 30 min, these were collected, washed with ethanol and ether, and dried over P_2O_5 under vacuum. Visible spectrum: ϵ_{485}(max) 83.0 (R = CH_3, 0.1 M NaOH).

$[(NH_3)_5CoN{=}C(NH_2)N(CH_3)_2](ClO_4)_2\cdot H_2O$ and $[(NH_3)_5CoN{=}C(NH_2)N(CH_3)_2](CF_3SO_3)_2\cdot H_2O$. This material was prepared exactly as described for the amidines except one treatment with NH_3(l) was sufficient, and the product was recrystallized from a minimum volume of aqueous Tris (0.02 M) with either aqueous $NaCF_3SO_3$ or $NaClO_4$ as the precipitant to afford deep burgundy crystals, which were air dried (each was a monohydrate; ^{1}H NMR spectroscopy in dry Me_2SO). Visible spectrum: ϵ_{511}(max) 102.0 (0.1 M Tris).

Attempts to prepare the methyl amidine and dimethylguanidine complexes directly from the free ligands with use of standard synthetic practices yielded only $[(NH_3)_5CoOH](ClO_4)_2$.

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Registry No. $[(NH_3)_5CoNCN(CH_3)_2](ClO_4)_3$, 123881-63-0; $[(NH_3)_5CoNCCH_3](ClO_4)_3$, 15663-50-0; $[(NH_3)_5CoNCCH{=}CH_2](ClO_4)_3$, 15648-92-7; $[(NH_3)_5CoNCC_6H_5](ClO_4)_3$, 38363-82-5; $[(NH_3)_5CoNCC_6H_4$-*o*-$NO_2](ClO_4)_3$, 84935-04-6; $[(NH_3)_5CoNCC_6H_4$-*p*-$F](ClO_4)_3$, 123881-65-2; $[(NH_3)_5CoNH{=}C(NH_2)N(CH_3)_2](ClO_4)_3$, 123881-67-4; $[(NH_3)_5CoNH{=}C(NH_2)CH_3](ClO_4)_3$, 123881-69-6; $[(NH_3)_5CoNH{=}C(NH_2)CH{=}CH_2](ClO_4)_3$, 123881-71-0; $[(NH_3)_5CoNH{=}C(NH_2)C_6H_5](ClO_4)_3$, 123881-73-2; $[(NH_3)_5CoNH{=}C(NH_2)C_6H_4$-*o*-$NO_2](ClO_4)_3$, 123881-75-4; $[(NH_3)_5CoNH{=}C(NH_2)C_6H_4$-*p*-$F](ClO_4)_3$, 123881-77-6; $[(NH_3)_5CoNH{=}C(NH)CH_3](ClO_4)_2$, 123881-79-8; $[(NH_3)_5CoNH{=}C(NH)C_6H_4$-*o*-$NO_2](ClO_4)_2$, 123881-81-2; $[(NH_3)_5CoN{=}C(NH_2)N(CH_3)_2](ClO_4)_2$, 123881-83-4; $[(NH_3)_5CoN{=}C(NH_2)N(CH_3)_2](CF_3SO_3)_2$, 123881-84-5; NH_3, 7664-41-7; $NCN(CH_2)$, 1467-79-4; $NCCH_3$, 75-05-8; $NCCH{=}CH_2$, 107-13-1; NCC_6H_5, 100-47-0; NCC_6H_4-*o*-NO_2, 612-24-8; NCC_6H_4-*p*-F, 1194-02-1; $NH{=}C(NH_2)CH_3$, 143-37-3; $NH{=}C(NH_2)C_6H_4$-*o*-NO_2, 88718-94-9; $NH{=}C(NH_2)N(CH_3)_2$, 6145-42-2.

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Contribution from the Departments of Chemistry,
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Synthesis, Crystal and Molecular Structure, and Magnetic Properties of Bis[tris(μ-3,5-diamino-1,2,4-triazole-N^1,N^2)tris(thiocyanato-*N*)nickel(II)]nickel(II) Hexahydrate

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1,2,4-Triazoles have been actively investigated as versatile ligands that can yield polynuclear metal complexes with interesting magnetic properties.[2-7] In particular, it was found that three 1,2,4-triazoles can bridge between two metal ions, yielding dimeric and trinuclear species.[6,7] In order to prevent such a coordination and to favor the formation of thiocyanate bridges, Reedijk et al.[8] successfully used the strategy to employ bulky 3,5-disubstituted 1,2,4-triazoles. In particular, they isolated a compound of formula $Ni_3(detrH)_6(NCS)_6\cdot 2H_2O$ (detrH = 3,5-diethyl-1,2,4-triazole), in which the central and terminal ions are bridged by two triazoles and one thiocyanate ion, while the terminal nickel ions complete their octahedral coordination with one triazole and two thiocyanate atoms. We have now found that using 3,5-diamino-1,2,4-triazole, guanazole, as a ligand yields a compound of formula $Ni_3(guanazole)_6(NCS)_6\cdot 6H_2O$, which, notwithstanding the close similarity in the formula to $Ni_3(detrH)_6(NCS)_6\cdot 2H_2O$, has three bridging guanazoles between the internal and terminal nickel ions, and we report here its crystal structure and magnetic properties in order to compare them to those of $Ni_3(detrH)_6(NCS)_6\cdot 2H_2O$.

Experimental Section

Materials. Nickel(II) thiocyanate was prepared as reported in the literature.[9] 3,5-Diamino-1,2,4-triazole (guanazole) was used as the commercially available compound.

Synthesis. The metal salt (1 mmol) dissolved in water (20 mL) was added to the ligand (3 mmol) dissolved in water (6 mL). A very slow evaporation gives blue crystals suitable for X-ray data collection.

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