Table II

Angles (Deg)

A	B	C	angle
Mo(2)	Mo(1)	N(4)	101.8 (1)
Mo(2)	Mo(1)	N(10)	102.1 (1)
Mo(2)	Mo(1)	N(16)	102.1 (1)
N(4)	Mo(1)	N(10)	116.5 (1)
N(4)	Mo(1)	N(16)	114.7 (1)
N(10)	Mo(1)	N(16)	116.1 (1)
Mo(1)	Mo(2)	N(7)	102.2 (1)
Mo(1)	Mo(2)	N(13)	101.8 (1)
Mo(1)	Mo(2)	N(19)	101.5 (1)
N(7)	Mo(2)	N(13)	115.5 (1)
N(7)	Mo(2)	N(19)	114.0 (1)
N(13)	Mo(2)	N(19)	118.3 (1)
Mo(1)	N(4)	C(3)	115.5 (2)
Mo(1)	N(4)	C(5)	131.0 (2)
C(3)	N(4)	C(5)	111.4 (2)
Mo(2)	N(7)	C(6)	130.8 (2)
Mo(2)	N(7)	C(8)	115.6 (2)
C(6)	N(7)	C(8)	111.4 (2)
Mo(1)	N(10)	C(9)	114.7 (2)
Mo(1)	N(10)	C(11)	132.3 (2)
C(9)	N(10)	C(11)	110.7 (2)
Mo(2)	N(13)	C(12)	131.8 (2)
Mo(2)	N(13)	C(14)	115.8 (2)
C(12)	N(13)	C(14)	110.9 (2)
Mo(1)	N(16)	C(15)	115.7 (2)
Mo(1)	N(16)	C(17)	132.8 (2)
C(15)	N(16)	C(17)	110.4 (2)
Mo(2)	N(19)	C(18)	129.4 (2)
Mo(2)	N(19)	C(20)	116.1 (2)
C(18)	N(19)	C(20)	111.5 (2)
N(4)	C(5)	C(6)	115.1 (2)
N(7)	C(6)	C(5)	114.2 (2)
N(10)	C(11)	C(12)	115.2 (2)
N(13)	C(12)	C(11)	116.1 (2)
N(16)	C(17)	C(18)	114.7 (2)
N(19)	C(18)	C(17)	115.0 (2)

Torsion Angles (Deg)

N(4)	Mo(1)	Mo(2)	N(7)	11.8 (2)
N(10)	Mo(1)	Mo(2)	N(13)	10.7 (2)
N(16)	Mo(1)	Mo(2)	N(19)	12.6 (2)

A single-crystal X-ray study[7] confirmed the triply bridged structure, shown in Figure 1. This view of the molecule emphasizes the twist-boat nature of the six-membered ring formed by each $Mo_2N_2C_2$ unit. In Figure 2 the molecule is viewed down the Mo–Mo axis which emphasizes the near-eclipsed geometry of the Mo_2N_6 moiety. Pertinent bond distances and bond angles are given in Tables I and II, respectively.

A comparison between the structures of this new compound and $Mo_2(NMe_2)_6$[8] reveals striking similarities. In both compounds each Mo–NC$_2$ unit is virtually planar with the planes aligned along the Mo–Mo axis and the Mo–N distances are within the range 1.96–1.98 Å indicative of nitrogen-to-molybdenum π bonding. The close similarity in nitrogen-to-molybdenum bonding is also revealed in a comparison of the Mo–Mo–N and proximal (α) and distal (β) Mo–N–C angles. These are given in Table III. It is reasonable to conclude that ligand-to-metal bonding is virtually identical in the two compounds.

Table III. Summary of Angles (Degrees) Associated with the $Mo_2N_6C_{12}$ Skeletons of the $Mo_2(NMe_2)_6$ and $Mo_2(MeNCH_2CH_2NMe)_3$ Molecules

	Mo_2-$(NMe_2)_6$	Mo_2-$(MeNCH_2CH_2NMe)_3$
Mo–Mo–N	103.7 ± 0.3	101.8 ± 0.4
Mo–N–C (α)	133.4 ± 1.2	131.8 ± 1.0
Mo–N–C (β)	116.3 ± 0.3	115.7 ± 0.2

The unit cell of $Mo_2(NMe_2)_6$ contains two crystallographically independent molecules which yield two Mo-to-Mo distances, 2.211 (2) and 2.217 (2) Å. The Mo-to-Mo distance in $Mo_2(MeNCH_2CH_2NMe)_3$ is 2.190 (1) Å, which is significantly shorter by 0.02 Å. Whether this implies a significantly stronger metal-to-metal bond is a matter for further speculation. The known Mo-to-Mo distances in the staggered ethane-like Mo_2X_6 molecules span the range 2.167–2.222 Å, found for X = CH_2SiMe_3[9] and OCH_2CMe_3,[10] respectively. Our interpretation of the present finding is that the Mo-to-Mo triple bond is not particularly perturbed by the rotational conformation of the Mo_2N_6 skeleton.

Registry No. $Mo_2(MeNCH_2CH_2NMe)_3$, 74331-59-2; 1,2-$Mo_2Cl_2(NMe_2)_4$, 63301-82-6.

Supplementary Material Available: A table of observed and calculated structure factors (30 pages). Ordering information is given on any current masthead page. The complete report, MSC Report 7965, is available upon request in microfiche form only from the Indiana University Chemistry Library.

(7) Crystal data were collected at −175 ± 2 °C with the use of a gaseous-nitrogen cold stream and locally constructed goniostat system: triclinic, space group $P\bar{1}$ with a = 12.036 (3), b = 9.480 (3), c = 8.783 (2) Å; α = 107.94 (2), β = 100.56 (1), γ = 100.65 (1)°; Z = 2; d_{calcd} = 1.65 g cm^{-3}. Of 3215 unique structure amplitudes, the 3142 having $F > \sigma(F)$ were used in the refinement which included anisotropic thermal parameters for all nonhydrogen atoms. Final residuals were $R(F)$ = 0.025 and $R_w(F)$ = 0.041. All hydrogen atoms were located and refined with isotropic thermal parameters.

(8) Chisholm, M. H.; Cotton, F. A.; Frenz, B. A.; Reichert, W. W.; Shive, L. W.; Stults, B. R. *J. Am. Chem. Soc.* **1976**, *98*, 4469.

(9) Huq, F.; Mowat, W.; Shortland, A.; Skapski, A. C.; Wilkinson, G. *J. Chem. Soc. D* **1971**, 1071.
(10) Chisholm, M. H.; Cotton, F. A.; Murillo, C. A.; Reichert, W. W. *Inorg. Chem.* **1977**, *16*, 1801.

Contribution from the Institute for Chemical Research, Kyoto University, Uji, 611 Japan

Alkali-Metal-Ion Catalysis of the Electron-Transfer Reaction between 1-Propyl-3-carbamoyl-1,4-dihydropyridine and Hexacyanoferrate(III). A Linear Relationship Involving Catalytic Activity

T. Okamoto,* A. Ohno, and S. Oka

The rates of electron-transfer reaction between two ions or complexes have long been known to be influenced by the concentration and identity of supporting electrolytes.[1] Although less sensitive than ion–ion reactions, the reaction between an ion and a neutral molecule is also influenced by metal ions but in an unpredictable manner at present.[2] We are reporting here the electron-transfer reaction of *N*-propyl-

(1) J. C. Sheppard and A. C. Wahl, *J. Am. Chem. Soc.*, **79**, 1020 (1957); A. C. Wahl, *Z. Elektrochem.*, **60**, 90 (1960); M. Shopper, G. Ron, A. Lowentein, and G. Navon, *Inorg. Chem.*, **4**, 362 (1965); D. V. S. Jain and F. S. Nandel, *J. Chem. Soc., Dalton Trans.*, 949 (1977); F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions", 2nd ed., Wiley, New York, 1967, Chapter 6.
(2) F. C. Adam and S. I. Waissman, *J. Am. Chem. Soc.*, **80**, 1518 (1958); N. Hirota and S. I. Waissman, *ibid.*, **86**, 2537 (1964); R. L. Ward and S. I. Waissman, *ibid.*, **79**, 2086 (1957).

Table I. Influence of Salts on the Rate Constant

chloride	$10^{-2}k_{cat}$, $s^{-1} M^{-1}$	$k_0{}'$,[a] $s^{-1} M^{-1}$	$10^{24}\alpha$,[c] cm^3
Li	0	30.8 ± 0.8	0.03
Na	8.1 ± 0.2	29.6 ± 0.2	0.19
K	14.9 ± 0.8	(20.4 ± 0.9)[b]	0.89
Rb	23.0 ± 1.1	29.4 ± 0.7	1.50
Cs	83.1 ± 7.0	30.1 ± 3.2	2.60
Et$_4$N	-2.8 ± 0.6	29.7 ± 0.5	

[a] Calculated value 30.1. [b] k_0. [c] From ref 8.

1,4-dihydronicotinamide (PNAH) with hexacyanoferrate(III) catalyzed by alkali-metal ions.[3]

$$H_2C \; \; \text{(structure)} + 2Fe(CN)_6^{3-} \xrightarrow{M^+} \; \text{(structure)} +$$

$$2Fe(CN)_6^{4-} + H^+$$
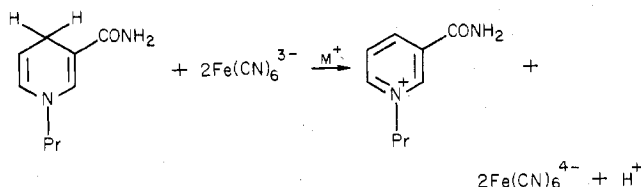
The catalytic activity decreases in the order $Cs^+ > Rb^+ > K^+ > Na^+ > Li^+ \geq 0$, bearing a linear relationship between the polarizabilities of the alkali-metal ions and the logarithms of the apparent catalytic constants, presenting the first linear free energy relationship pertaining to alkali-metal-ion catalysis.
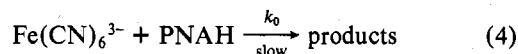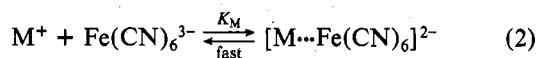
Experimental Section

Inorganic salts were analytical grade reagents and were used without further purification. Kinetic measurements were recorded on a Union Giken SM 401 spectrophotometer monitoring the absorbance change at 356 nm after injection of a solution of PNAH into a 10-mm optical cuvette which contained a solution of $Fe(CN)_6^{3-}$ and inorganic salts at 298.1 ± 0.1 K under nitrogen.[4] The concentrations examined were as follows: $K_3Fe(CN)_6$, 5.00×10^{-4} M; K_2CO_3, 2.50×10^{-3} M; PNAH, 2.50×10^{-5} M; and alkali-metal or tetraethylammonium chloride, 1.50×10^{-2} to 1.00×10^{-3} M in 80% aqueous methanol.

Results and Discussion

The observed second-order rate constants (k_{obsd}) in the presence of alkali-metal chlorides or tetraethylammonium chloride are given with the correlation factors exceeding 0.999 for over 90% of each reaction. A typical example with [LiCl] $= 0.140 \times 10^{-2}$ M has a rate constant of 31.6 ± 0.2 s^{-1} M^{-1} with the correlation factor of 0.9997. There are generally linear correlations between rate constants and the concentrations of cations but a leveling off of the rate is observed at the high concentration of cesium ion.

$$-d[PNAH]/dt = k_{obsd}[Fe(CN)_6^{3-}][PNAH] \quad (1)$$

The mechanism of the reaction is proposed as in eq 2–4, where

$$M^+ + Fe(CN)_6^{3-} \underset{fast}{\overset{K_M}{\rightleftharpoons}} [M\cdots Fe(CN)_6]^{2-} \quad (2)$$

$$[M\cdots Fe(CN)_6]^{2-} + PNAH \xrightarrow{k_M}_{slow} products \quad (3)$$

$$Fe(CN)_6^{3-} + PNAH \xrightarrow{k_0}_{slow} products \quad (4)$$

K_M is the equilibrium constant of the formation of cation–$Fe(CN)_6^{3-}$ complex[5] and k_M and k_0 show the rate constants of the catalyzed and the uncatalyzed electron-transfer reactions, respectively.

The observed rate constant is expressed by eq 5. Assuming that the term of $K_M[M^+]$ is negligible compared with unity
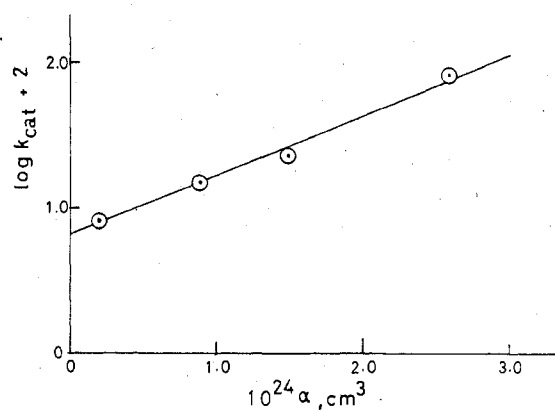

Figure 1. Plot of log k_{cat} for reaction of PNAH with $Fe(CN)_6^{3-}$ vs. polarizability of alkali-metal ion (Na^+, K^+, Rb^+, Cs^+).

in the denominator, we can rewrite eq 5 as eq 6, where k_{cat} represents the apparent catalytic constant of metal-catalyzed reaction. Since we observed linear relationships between the

$$k_{obsd} = \frac{k_0 + k_M K_M[M^+]}{1 + K_M[M^+]} \quad (5)$$

$$k_{obsd} = k_0 + k_M K_M[M^+] = k_0 + k_{cat}[M^+] \quad (6)$$

concentrations of metal ions and the apparent rate constants, the above requirement must be satisfied for all cations except cesium ion throughout the concentration ranges examined. Thus k_{cat} is estimated from the slope of the plot of k_{obsd} against the concentration of metal ion (Table I). Ionic strength effects do not contribute significantly to the reaction rate. As the insensitivity of the rate to the change of ionic strength is known by the Olson–Simonson rule for electron-transfer reactions between two like charges,[6,7] the present results show that the rule is effective also for the system containing neutral molecules as well.

The observed acceleration is not accounted for by the bulkiness[9] or dehydration energy of ions.[10] A plausible explanation of the present result is that the alkali-metal ion catalyzes the electron-transfer step itself as a polarizable species which behaves as an electron mediator. Tetraethylammonium ion, which has a larger association constant (K_M) than alkali-metal ions[5] but does not mediate electron transfer, has a small negative catalytic constant. Roughly speaking, the contribution of K_M to the overall catalytic constant would be small because the reported K_M in water does not vary much from Na^+ to Cs^+ (about threefold)[5] and because the difference is expected to be less in a less polar solvent used in the present work, whereas the change of k_{cat} from Na^+ to Cs^+ is more than 10-fold. If we assume K_M is nearly constant for these cations, then a linear free energy relationship could be expected between the catalytic constant and the effectiveness as an electron-mediator, for which the polarizability of an ion could be accepted as the index. The resultant plot of the logarithms of k_{cat} against the polarizabilities of the cations (α) is shown in Figure 1, suggesting a fairly good relationship of linear free energy. However, it should be noted here that the observed medium effects are not necessarily characteristic of the electron-transfer reaction because salt effects in mixed solvents show complex behavior[11] and these results might be ration-

(3) Preliminary communication: T. Okamoto, A. Ohno, and S. Oka, *J. Chem. Soc., Chem. Commun.*, 785 (1977).
(4) See the previous paper for details of the mechanism of this reaction: T. Okamoto, A. Ohno, and S. Oka, *Bull. Chem. Soc. Jpn.*, **53**, 330 (1980).
(5) L. G. Sillen and A. E. Martell, *Chem. Soc., Spec. Publ., Suppl. No. 1, No. 25*, 50 (1971).

(6) A. R. Olson and T. R. Simonson, *J. Chem. Phys.*, **17**, 1167 (1949).
(7) R. J. Campion, C. F. Deck, P. King, Jr., and A. C. Wahl, *Inorg. Chem.*, **6**, 672 (1967).
(8) C. N. R. Rao, "A Hand Book of Chemistry and Physics", Affiliated East-West Press, New Dehli, 1967, p 234 (cited by D. V. S. Jain and F. S. Nandel, *J. Chem. Soc., Dalton Trans.*, 949 (1977)).
(9) E. R. Nightingale, Jr., *J. Phys. Chem.*, **63**, 1381 (1959).
(10) H. F. Halliwell and S. C. Nyburg, *Trans. Faraday Soc.*, **59**, 1126 (1963).

alized as reflecting differences in the degree of ion-pairing and salting-out effects.[12]

Supplementary Material Available: A listing of k_{obsd} at various concentrations of alkali-metal and tetraethylammonium chlorides (1 page). Ordering information is given on any current masthead page.

(11) J. H. Gordon, "The Organic Chemistry of Electrolyte Solutions", Wiley, New York, 1975, Chapters 1 and 3.
(12) The authors wish to thank a reviewer for suggesting the possibility.

Contribution from the Department of Chemistry,
Faculty of Science, Tohoku University,
Aoba, Aramaki, Sendai 980, Japan

Syntheses and Properties of Pentaamminecobalt(III) Complexes Containing *N*-Methyl-, *N*,*N*-Dimethyl-, and *N*,*N'*-Dimethylethylenediamine and (2-Aminoethyl)trimethylammonium Ion

Hiroshi Ogino,* Yukiko Orihara, and Nobuyuki Tanaka

In a recent article, it was concluded that an intense absorption in the ultraviolet region observed for [Co(NH$_3$)$_5$-(en)]$^{3+}$ was a charge-transfer band due to the intramolecular hydrogen bonding between a free amino group and an NH proton on the cobalt(III) center:[1] There are two possible modes of hydrogen bonding as shown in Chart I. In this work, pentaamminecobalt(III) complexes containing the following analogues of ethylenediamine were synthesized and their pK_a values were determined: CH$_3$NHCH$_2$CH$_2$NH$_2$ (meen), (CH$_3$)$_2$NCH$_2$CH$_2$NH$_2$ (*asym*-dimeen), CH$_3$NHCH$_2$CH$_2$N-HCH$_3$ (*sym*-dimeen), and (CH$_3$)$_3$NCH$_2$CH$_2$NH$_2^+$ (tmen$^+$). The spectral features of these complexes are discussed in terms of the hydrogen bonding as mentioned above.

Experimental Section

A. Materials. The ligands meen, *asym*-dimeen, and *sym*-dimeen were obtained from Tokyo Kasei Co. (The diamines will hereafter be referred to as N-N.) The ligand tmenBr·HClO$_4$ was prepared according to the literature.[2]

B. Preparation of Complexes. The complexes [Co(NH$_3$)$_5$(N-N-H)](ClO$_4$)$_4$ and [Co(NH$_3$)$_5$(tmen)](ClO$_4$)$_4$ were prepared in a way similar to that which has been reported for the preparation of [Co-(NH$_3$)$_5$(enH)](ClO$_4$)$_4$.[3] The analytical data for the complexes prepared in this work are given in Table I.[4]

Caution! Although no explosions were encountered in the present study, perchlorate salts should be handled with appropriate precautions.

Products of the Reaction of [Co(H$_2$O)(NH$_3$)$_5$]X$_3$ (X = ClO$_4^-$ or BF$_4^-$) with N-N. N-N = meen. Equimolar amounts (0.01 mol each) of [Co(H$_2$O)(NH$_3$)$_5$]X$_3$ and meen were added to 250 mL of dimethyl sulfoxide (Me$_2$SO). The solution was kept at 85 °C for 15 min. The resulting solution was neutralized with HCl and diluted to 1 L with water. This was poured into a column (3 × 25 cm) of SP-Sephadex C-25 (SPC). The column showed three bands: red at the bottom, yellow in the middle, and yellowish orange at the top. The first and second species were eluted together with a 0.4 M KBr solution and were characterized as a mixture of [Co(H$_2$O)(NH$_3$)$_5$]$^{3+}$, [Co-(NH$_3$)$_6$]$^{3+}$, [Co(NH$_3$)$_4$(meen)]$^{3+}$, [Co(NH$_3$)$_2$(meen)$_2$]$^{3+}$, and [Co-(meen)$_3$]$^{3+}$.[5] The yellowish orange species was eluted with a 0.6 M

(1) Ogino, H. *Inorg. Chem.* **1980**, *19*, 1619.
(2) Lin, C.-T.; Rorabacher, D. B. *Inorg. Chem.* **1973**, *12*, 2402.
(3) Ogino, H. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 2459.
(4) Supplementary material.

Chart I
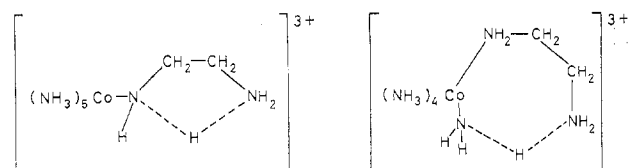
Table II. pK_a Values of [Co(NH$_3$)$_5$(N-NH)]$^{4+}$, HN-NH^{2+}, and Htmen^{2+} at 25 °C[a]

compd	pK_{a1}	pK_a	pK_{a2}
[Co(NH$_3$)$_5$(enH)]$^{4+}$ [b]		7.52 ± 0.03	
[Co(NH$_3$)$_5$(meenH)]$^{4+}$		7.88 ± 0.03	
[Co(NH$_3$)$_5$-(*asym*-dimeenH)]$^{4+}$		7.24 ± 0.03	
H$_2$en^{2+} [b]	7.15 ± 0.03		9.87 ± 0.04
H$_2$meen^{2+}	7.40 ± 0.03		10.21 ± 0.04
H$_2$(*asym*-dimeen)$^{2+}$	6.81 ± 0.03		9.85 ± 0.04
H$_2$(*sym*-dimeen)$^{2+}$	7.17 ± 0.03		10.07 ± 0.04
Htmen^{2+} [c]		7.1	

[a] At I = 0.1 (NaCl), unless otherwise indicated. [b] From ref 1. [c] From ref 2; at I = 0.007 (NaClO$_4$).

KBr solution. The eluate was reloaded on an SPC column. After the column was washed with a 0.3 M HCl solution, the adsorbed species was eluted with a 1 M LiClO$_4$ solution of pH 2.5 (adjusted with HClO$_4$). The eluate was evaporated to dryness. The remaining solid LiClO$_4$·3H$_2$O was washed out with ethanol. Crystals of [Co-(NH$_3$)$_5$(meenH)](ClO$_4$)$_4$ remained; yield 0.4 g.

N-N = *asym*-dimeen and *sym*-dimeen. Equimolar amounts (0.01 mol each) of [Co(H$_2$O)(NH$_3$)$_5$]X$_3$ and *asym*- or *sym*-dimeen were added to 1 L of Me$_2$SO. The solution was treated in the way described for the meen system. Four bands were observed on an SPC column. The lowest and the second species were identified as Co^{2+} and [Co-(H$_2$O)(NH$_3$)$_5$]$^{3+}$, respectively. The third band was found to contain [Co(NH$_3$)$_6$]$^{3+}$ and [Co(NH$_3$)$_4$(dimeen)]$^{3+}$.[6] The fourth species was eluted with a 0.6 M KBr solution. The eluate from the *asym*-dimeen system was reloaded on an SPC column. The adsorbed species was treated in the way described for the isolation of [Co(NH$_3$)$_5$-(meenH)](ClO$_4$)$_4$. Orange crystals of [Co(NH$_3$)$_5$(*asym*-dimeenH)](ClO$_4$)$_4$·0.2HClO$_4$·2H$_2$O were obtained; yield 0.23 g. Although the solid sample from the fourth eluate of the *sym*-dimeen was not isolated because of the very low yield, the species was concluded to be [Co(NH$_3$)$_5$(*sym*-dimeenH)]$^{4+}$ from the flow rate on the SPC column[7] and the electronic spectrum.

N-N = tmen$^+$. To 200 mL of Me$_2$SO solution containing 0.01 mol of [Co(H$_2$O)(NH$_3$)$_5$](BF$_4$)$_3$ were added 3.6 mmol of tmenBr·HClO$_4$, 0.5 g of active carbon, and 3 mL of triethylamine. The solution was kept at 85 °C for 15 min. After removal of the active carbon by filtration, the solution was treated in the way described for the meen system. The SPC column showed five bands: Co^{2+}, [CoBr(NH$_3$)$_5$]$^{2+}$, [Co(H$_2$O)(NH$_3$)$_5$]$^{3+}$, [Co(NH$_3$)$_6$]$^{3+}$, and [Co(NH$_3$)$_5$(tmen)]$^{4+}$ from the bottom to the top of the column. After the former four species had been eluted out, the uppermost species was eluted with a 1 M NaCl solution. This eluate was treated in the way described for the isolation of [Co(NH$_3$)$_5$(meenH)](ClO$_4$)$_4$. Crystals of [Co(NH$_3$)$_5$-(tmen)](ClO$_4$)$_4$ were obtained; yield 0.06 g.

C. Determination of pK_a Values and Measurements of Electronic Spectra. For determining the pK_a values, pH titrations were made with a standard sodium hydroxide or hydrochloric acid solution as described previously.[1] The measurements of electronic spectra were made with a Union-Giken SM-401 spectrophotometer, also reported previously.[1]

(5) These species were separated as follows: The concentration of the eluate gave solid [Co(NH$_3$)$_6$]Br$_3$. The filtrate was reloaded on an SPC column. Four bands appeared by elution with 0.01–0.025 M Na$_4$P$_2$O$_7$ solutions. The order of the elution was [Co(H$_2$O)(NH$_3$)$_5$]$^{3+}$, [Co-(meen)$_3$]$^{3+}$, [Co(NH$_3$)$_4$(meen)]$^{3+}$, and [Co(NH$_3$)$_2$(meen)$_2$]$^{3+}$.
(6) The concentration of the eluate gave solid [Co(NH$_3$)$_6$]Br$_3$. The filtrate was reloaded on an SPC column. The adsorbed species was eluted with a 0.5 M HCl solution. The concentration of the eluate gave solid [Co(NH$_3$)$_4$(dimeen)]Cl$_3$·nH$_2$O.
(7) Ogino, H.; Fujita, J. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 1836.