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Preparation and NMR Spectra of Hexacoordinate Metal Complexes of Mono(*N*-ethylethanediamine) and Mono(*N*-benzylethanediamine) and Crystal Structure of $[Co(NH_3)_4(N\text{-benzylethanediamine})](NO_3)_3\cdot 1.5H_2O$

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Mono *N*-ethylethanediamine and *N*-benzylethanediamine complexes of Co(III), Fe(II), and Fe(III) with four cyano or ammine groups were prepared. Their ^{1}H NMR spectra were measured to determine the conformation of *N*-ethyl and *N*-benzyl groups. These *N*-alkyl groups take pseudo-equatorial orientation at the coordinated secondary amine. The most preferred conformation is that the methyl and phenyl groups are anti with respect to the central metal ions. The crystal structure parameters of $[Co(NH_3)_4(N\text{-benzylethanediamine})](NO_3)_3\cdot 1.5H_2O$ were determined: $P2_1$, $Z=2$, $a=8.639(3)$, $b=21.240(3)$, $c=10.897(2)$ Å, $\beta=94.11(1)°$. The crystallographically independent Co complex cations had opposite absolute configuration around coordinated secondary amine sites and the benzyl groups are anti to the cobalt atom.

The stereochemistry of bidentate chelate rings has been studied by various methods. The NMR methods have provided strong clues about molecular geometry through the dihedral angle dependence of the three-bond vicinal coupling constant, $^3J_{\text{H–H}}$, in the H–C–C–H fragment.[1] The conformations of five-membered chelate rings in metal complexes in solutions are now predictable on the assumption that an ethanediamine chelate ring with substituent bonded to the carbon atoms prefers the substituent groups in equatorial dispositions. The dispositions of the substituents bonded to the nitrogen donor atoms are less clear, due to the smaller difference in energy between axial and equatorial dispositions. These substituents will take predominantly an equatorial position in octahedral complexes.[1] But isomers with equatorial and axial dispositions have nearly the same energy in square-coplanar complexes and two forms have been isolated and analyzed for $[Pt(\text{Me-}S\text{-pn})Cl_2]$, where Me-*S*-pn represents *S*-2-methyl-1,4-diazapentane.[2] The substitution of both chloro ligands with 2,2′-bipyridyl (bpy) or 1,10-phenanthroline (phen) in square-coplanar complexes forces the substituents at the nitrogen atom to take an axial disposition through interligand non-bonding interaction between 6,6′-hydrogens of bpy or 2,9-hydrogens of phen and the substituents.[3]

The analysis of the stereochemistry of *N*-alkylethanediamines, however, has been done with an *N*-methyl as the *N*-alkyl group, such as *N*-methylethanediamine (Meen) and *N*,*N*′-dimethylethanediamine (s-Me$_2$en),[4] but not often with an *N*-alkyl group higher than methyl.[5]

Using a 100 MHz spectrometer we found that *N*-ethylethanediamine (Eten) exhibits a complicated ^{1}H NMR spectrum due to severe overlapping signals when coordinated to tetracyanoferrate(II), in spite of the rather simple structure of the complex. To elucidate the structure of the chelate ring formed by Eten especially of its ethyl group, we prepared three mono(Eten) metal complexes: $[Co(CN)_4(\text{Eten})]^-$, $[Fe(CN)_4(\text{Eten})]^{2-}$, and $[Co(NH_3)_4(\text{Eten})]^{3+}$. Two cobalt(III) complexes of *N*-benzylethanediamine (Been) were also prepared and the stereochemistry of the chelate ring was analyzed by taking advantage of the magnetic effect of the phenyl ring on protons in proximity. The molecular structure of $[Co(NH_3)_4(\text{Been})]^{3+}$ has been examined by X-ray crystallography on $[Co(NH_3)_4(\text{Been})](NO_3)_3\cdot 1.5H_2O$.

Experimental

Materials. The following metal complexes for preparing the Eten and Been complexes were prepared according to the references: $K_3[CoCl(CN)_5]$, $K_3[CoBr(CN)_5]$,[7] and $[Co(NO_3)_2(NH_3)_4]NO_3$.[8] Eten and Been were purchased from Tokyo Kasei, and $Fe(ClO_4)_2\cdot 6H_2O$ from Alpha; they were used without further purification. Other reagents were purchased with the highest purity available and were used without further purification.

Preparation of Metal Complexes. $Na[Co(CN)_4(\text{Eten})]$: A mixture of $K_3[CoCl(CN)_5]$ (5 g, 0.0146 mol), Eten (5 g, 0.0567 mol), and water (20 mL) was stirred at 65 °C for 7 h. The resultant mixture was poured into a 450 mL portion of methanol; then separated white precipitates were removed by filtration. The filtrate was concentrated with a rotatory evaporator. The residue was again mixed with 200 mL of methanol and the undissolved white solid was removed by filtration. The filtrate was concentrated and dissolved in 30 mL of water. The yellow aqueous solution was applied to a Dowex 1X8 anion exchange column ($\phi 3\times 10$ cm). The absorbed mixture was eluted with water (2 L), 0.01 M HCl (1 M=1 mol dm^{-3}, 2 L), 0.1 M HCl (2 L), and 0.2 M HCl (2 L) successively. The pale yellow band eluted with 0.2 M HCl was collected and concentrated to near dryness and then was dissolved in 15 mL portion of water. The residue after neutralization with 1 M NaOH was dissolved in a mixture of water (2 mL), ethanol (22 mL), and ether (8 mL). To this solution, isopropyl ether (20 mL) was added. Separated yellow precipitates were collected on a filter and stored in vacuo. Yield, 488 mg. Anal. Calcd for $Na[Co(CN)_4(C_4H_{12}N_2)]$: C, 35.05; H, 4.41; N, 30.66%. Found: C, 34.71; H, 4.86; N, 30.79%.

$Na[Co(CN)_4(Been)]\cdot 2H_2O$: A mixture of $K_3[CoBr(CN)_5]$ (3.86 g, 0.01 mol) and Been (1.50 g, 0.01 mol) in 10 mL water was heated at 80 °C for 16 h. The resultant orange solution was concentrated to dryness with a rotatory evaporator. The yellow-orange residue was extracted with a 30 mL portion of methanol twice under reflux. The methanol extract was concentrated to near dryness; ether (30 mL) was added to the residue and ether-soluble materials were discarded by decantation. The mixture was taken into a 20 mL portion of water and the mixture was filtered. The yellow filtrate was placed on the top of a Dowex 1X8 column ($\phi 3\times 10$ cm) and washed with 500 mL of water and 0.4 M hydrochloric acid successively. The pale yellow fraction which was eluted with 2 M hydrochloric acid was combined and concentrated to dryness. The residue was dissolved into about 2 mL of water after neutralization with 1 M NaOH, filtered, and chromatographed with a Sephadex G15 column ($\phi 1.8\times 86$ cm), using water as the eluant. The fractions which have an absorption maximum at 358 nm were pooled and concentrated with a rotatory evaporator. The remaining yellow solid was dissolved into 2 mL of methanol and 1 mL of acetonitrile; 4 mL of ether was added to the mixture and the mixture was left to stand in a refrigerator overnight. Separated pale yellow crystals were collected on a filter and washed with ether. Yield, 160 mg. Anal. Calcd for $Na[Co(CN)_4(C_9H_{14}N_2)]\cdot 2H_2O$: C, 41.95; H, 4.87; N, 22.58%. Found: C, 41.66; H, 4.96; N, 22.58%.

$Na_2[Fe(CN)_4(Eten)]\cdot 0.5(CH_3OH)\cdot 0.5(NaClO_4)\cdot 3(H_2O)$: Into a three-necked flask, $Fe(ClO_4)_2\cdot 6H_2O$ (14.51 g, 0.04 mol) was placed; methanol (40 mL) was added to dissolve the solid material under nitrogen at 0 °C. Three equivalents of Eten (10. 60 g, 0.12 mol) in methanol (20 mL) and four equivalents of NaCN (7.85 g, 0.16 mol) in water (20 mL) were added successively to the Fe(II) solution under vigorous stirring. The resultant mixture was stirred for 1 h at 0 °C; then ethanol (100 mL) was added to precipitate the Fe(II) complex. The mixture was allowed to stand overnight at 0 °C. Separated yellow precipitates were collected on a filter and washed with ethanol (40 mL) and ether (10 mL) successively and then stored in vacuo.

The crude product was dissolved in 15 mL of water; undissolved materials were filtered off using Wako No. 5a filtration paper. To the filtrate, methanol (50 mL) and ethanol (100 mL) were added successively and the mixture was left to stand at room temperature overnight. Separated yellow crystals were collected on a filter and washed with ethanol (40 mL) and ether (10 mL) successively and then stored in vacuo. Yield. 9.92 g (58.3%). Anal. Calcd for $Na_2[Fe(CN)_4(C_4H_{12}N_2)]\text{-}0.5(CH_3OH)\cdot 0.5(NaClO_4)\cdot 3(H_2O)$: C, 24.00; H, 4.74; N, 19.76%. Found: C, 24.35; H, 5.13; N, 20.07%.

$[Co(NH_3)_4(Eten)](ClO_4)_2(NO_2)$: A mixture of $[Co(NO_3)_2(NH_3)_4](NO_3)\cdot H_2O$ (3.31 g, 0.01 mol) and Eten (0.88 g, 0.01 mol) in 30 mL of dimethylsulfoxide (DMSO) was stirred for 3 h at 65 °C. The mixture was poured into 200 mL of absolute ethanol. The separated orange-brown precipitates were collected on a filter. These precipitates (2.84 g) were dissolved in a mixture of water (12 mL) and two drops of acetic acid. This mixture was reduced in volume by heating on a hot plate and then cooled. Separated crystalline materials were collected on a filter; then their infrared spectrum was examined. After 3 cycles of these procedures, orange precipitates which showed sharp absorptions in the range between 1000 and 1200 cm^{-1} were obtained (the total volume: 1 mL). Yield, 921 mg.

This crude product was dissolved in water (4 mL) at 60 °C; then a mixture of $NaClO_4$ (1.22 g) and $NaNO_2$ (350 mg) in 10 mL of water was added. After the volume of this mixture was reduced to ca. 4 mL, the mixture was kept at room temperature. Separated crystals were collected on a filter; these were recrystallized from 2 mL of water and two drops of acetic acid. Anal. Calcd for $[Co(NH_3)_4(C_{14}H_{12}N_2)]\text{-}(ClO_4)_2(NO_2)$: C, 10.44; H, 5.26; N, 21.31%. Found: C, 10.45; H, 4.91; N, 21.46%.

$[Co(NH_3)_4(Been)](NO_3)_3\cdot 1.5H_2O$: A mixture of $[Co(NO_3)_2(NH_3)_4](NO_3)\cdot H_2O$ (2.95 g, 8.9 mmol) and Been (1.65 g, 10.8 mmol) in 5 mL of DMSO solution was gently stirred for 6 h at 60 °C. The mixture turned to a dark orange solution; then 40 mL of ethanol were added. Separated orange precipitates were collected on a filter, washed with ether and dried in vacuo (4.14 g). From the filtrate, pale pink precipitates were formed on addition of 60 mL of ethanol and these were also collected on a filter. Successive careful crystallization of these precipitates from water and a few drops of acetic acid by slow evaporation afforded plate crystals, which showed absorptions at 3190, 1626, 1389(v.s.), 828, and 705 cm^{-1} with KBr pellets. yield, 800 mg. Anal. Calcd for $[Co(NH_3)_4(C_9H_{14}N_2)](NO_3)_3\cdot 1.5H_2O$: C, 22.05; H, 5.96; N, 25.71%. Found: C, 22.45; H, 5.37; N, 26.29%.

Physical Measurements. ^{1}H NMR spectra of $[Fe(CN)_4(Eten)]^-$. Several attempts to isolate this complex ion from the mixture of oxidized products of $Na_2[Fe(CN)_4(Eten)]0.5CH_3OH\cdot 0.5NaClO_4\cdot 3H_2O$ were not successful, due to the high solubility of this compound. The ^{1}H NMR of $[Fe(CN)_4(Eten)]^-$ were recorded, therefore, with samples prepared in situ by addition of $Na_2S_2O_8$. The Fe(II) complex (63.6 mg) was dissolved into 430 mg of D_2O, followed by successive addition of DCl (37.5 mg) and $Na_2S_2O_8$ (116 mg). The resultant solution was transferred to an NMR sample tube and ^{1}H NMR spectrum was recorded on a JEOL FX-100 spectrometer within 10 min.

Before we assigned each signal, the Fe(II) complex was dissolved in pD 2.0 DCl–D_2O. As the oxidizing agent, various amounts of $K_3[Fe(CN)_6]$ were mixed; the ^{1}H NMR spectra were recorded within 10 min. The molar ratios of $K_3[Fe(CN)_6]$ to the Fe(II) complex were 0.001, 0.025, 0.042, and 0.093.

UV and visible absorption spectra were recorded with a

Shimadzu UV-210 spectrophotometer. Infrared spectra were recorded on a JASCO IRA2 spectrophotometer using Nujol mulls. ^{1}H NMR spectra were recorded on a JEOL GSX-400 spectrometer using sodium trimethylsilylpropionate-d_4 (TSP) as an internal standard. ^{13}C NMR spectra were recorded on a JEOL FX-100 spectrometer using dioxane as an internal standard.

X-Ray Crystallography. Crystals of $[Co(NH_3)_4(Been)](NO_3)_3 \cdot 1.5H_2O$ were grown by slow evaporation of the aqueous solution of the compound. Crystallographic data were collected as is summarized in Table 1. The unit cell parameters and the intensity data were measured on an Enraf–Nonius CAD-4 single-crystal diffractometer using graphite-monochromated Mo $K\alpha$ radiation. Unit cell parameters were obtained by a least-squres refinement of the values in the range between 3—50° of 25 carefully centered reflections chosen from different regions of the reciprocal space. Data were collected at 20±1 °C. The structures were solved and refined by the Enraf–Nonius SDP crystallgraphic computing package.[9] The structure amplitudes were obtained after the usual Lorentz and polarization reductions.[9] An empirical correction for absorption effects was applied.[9] The structure was solved by using conventional Patterson and Fourier techniques and refined by full-matrix least squares. In the last cycles of refinement, anisotropic thermal parameters were used for all the nonhydrogen atoms. The hydrogen atoms were clearly located in the final difference Fourier map, but not refined; those were placed at their geometrically calculated positions and included in the final structure calculation with their parameters fixed. The scattering factors were taken from Ref. 10 with the exceptions of those of the hydrogen atoms, which were taken from Ref. 11. Corrections for the real and imaginary components of anomalous dispersions were made. Final atomic coordinates are listed in Table 2. Selected bond distances and angles are reported in Tables 3 and 4. Lists of anisotropic thermal factors for nonhydrogen atoms, coordinates for hydrogen atoms, and F_o-F_c tables were deposited as Document No. 68008 at the Office of the Editor of Bull. Chem. Soc. Jpn.

Table 1. Experimental Data for the X-Ray Diffraction Study of $[Co(NH_3)_4(Been)](NO_3)_3 \cdot 1.5H_2O$

Formula	$C_{18}H_{58}N_{18}O_{21}Co_2$
Mol wt	980.631
Crystal system	Monoclinic
Space group	$P2_1$
a/Å	8.639(3)
b/Å	21.240(3)
c/Å	10.897(3)
β/°	94.11(1)
V/Å^3	1993.9(8)
Z	2
d_{calcd}/g cm^{-3}	1.63
d_{obsd}/g cm^{-3}	1.63
Crystal size/mm	0.42, 0.35, 0.04
Color	Orange
Habit	Plate
Scan type	ω–2θ
Radiation (Å)	Mo $K\alpha$ (0.71073)
Scan range 2θ/°	3.0—50
Temp/K	293
Data collcd	$h,k,\pm l$
No. of reflecns	3848
No. of reflecns used in calc	2738
$R^{a)}$	0.045
$R_w^{b)}$	0.047

a) $R=\sum||F_o|-|F_c||/\sum|F_o|$. b) $R_w=\{\sum w(|F_o|-|F_c|)^2/\sum wF_o^2\}^{1/2}$, $w=1$.

Results and Discussion

The structure of an N-alkyl-1,2-diamine chelate is described by a combination of the configuration of the asymmetric nitrogen center and the conformation of the five-membered chelate ring. In Fig. 1A, the possible structures with R-configuration at the nitrogen center are drawn schematically: The five-membered chelate ring takes either a δ or a λ *gauche* conformation with the N-alkyl group in the axial and equatorial disposition, respectively. The former arrangement (R,δ) is expected to be more stable than the latter (R,λ) for octahedral complexes, because the repulsion between the alkyl group and an apical ligand (Y) is weaker for the former.[1] For square-coplanar complexes, the apical ligand (Y) is absent and the energy difference between (R,δ) and (R,λ) arrangements is smaller than for octahedral complexes; both isomers are populated and isolated with N-methylpropanediamine when X is Cl^-.[2] But when X=1/2(bipy) or 1/2(phen), the interligand interaction between the conjugated diimine and the methyl group forced the methyl group to take an axial disposition.[3]

If the alkyl group is denoted as $-CH_2-R$, the orientation of R must be taken into account in order to specify the structure of the alkyl group unless R=H. The Newman projection looking down the CH_2–N bond reveals that there are three different staggered conformations defined by the torsion angle of M–N–C–R for each *gauche* form, as shown in Fig. 1B.

The stereochemistry of the coordinated N-alkyldiamine was investigated using metal complexes bearing one molecule of Eten or Been as ligand which shows resonances in the magnetic field higher than 5 ppm other than phenyl protons. The mono (Eten) and (Been) complexes were prepared as $[Co(NH_3)_4(Eten)]^{3+}$, $[Co(CN)_4(Eten)]^-$, $[Fe(CN)_4(Eten)]^{2-}$, $[Co(NH_3)_4(Been)]^{3+}$, and $[Co(CN)_4(Been)]^-$ by employing the methods for preparation of the corresponding ethanediamine complexes.[11] The tetracyanocobaltate(III) complex was purified by anion exchange column chromatography. Several attempts to crystallize $[Fe(CN)_4(Eten)]^-$ with several cations were not successful, due to its high solubility. The ^{1}H NMR spectrum of tetracyano(N-ethylethanediamine)ferrate(III) was recorded on a sample of the corresponding Fe(II) complexes oxidized by $Na_2S_2O_8$ or $[Fe(CN)_6]^{3-}$.

The visible spectra of these complexes were typical

Table 2. Positional Parameters and Thermal Parameters (Å^2) of Non H Atoms of [Co(NH$_3$)$_4$(Been)]-(NO$_3$)$_3$·1.5H$_2$O with esd's in Parentheses

Atom	x	y	z	B_{eq}
Co(1)	0.5014(1)	0.096(0)	0.4774(1)	2.12(2)
N(1)	0.4544(8)	0.0933(4)	0.2971(6)	3.4(2)
N(2)	0.3759(7)	0.1761(3)	0.4737(6)	2.2(1)
N(3)	0.5528(7)	0.0979(4)	0.6562(6)	3.1(1)
N(4)	0.6208(8)	0.0173(4)	0.4648(7)	3.3(2)
N(5)	0.6905(8)	0.1461(3)	0.4599(7)	2.8(1)
N(6)	0.3186(8)	0.0444(4)	0.5001(7)	3.1(2)
C(1)	0.379(1)	0.1539(4)	0.2557(7)	3.3(2)
C(2)	0.283(1)	0.1762(3)	0.3548(7)	3.5(2)
C(3)	0.283(1)	0.1900(5)	0.5798(8)	2.8(2)
C(4)	0.197(1)	0.2519(5)	0.567(1)	2.3(2)
C(5)	0.271(1)	0.3080(5)	0.5888(9)	3.5(2)
C(6)	0.196(1)	0.3648(5)	0.5772(9)	4.6(2)
C(7)	0.038(1)	0.3663(5)	0.540(1)	4.4(2)
C(8)	−0.036(1)	0.3104(5)	0.5171(8)	4.0(2)
C(9)	0.038(1)	0.2534(5)	0.5283(9)	4.1(2)
Co(2)	0.0114(1)	0.40470(6)	0.0207(1)	2.32(2)
N(11)	0.0422(8)	0.3967(3)	0.1986(6)	2.6(1)
N(12)	0.139(1)	0.3264(3)	0.0147(7)	3.7(2)
N(13)	−0.021(1)	0.4107(4)	−0.1593(6)	3.9(2)
N(14)	−0.1199(8)	0.4790(3)	0.0384(6)	2.7(1)
N(15)	0.1963(9)	0.4606(4)	0.0170(8)	4.0(2)
N(16)	−0.1749(9)	0.3506(4)	0.0202(7)	3.2(2)
C(11)	0.144(1)	0.3436(5)	0.2356(8)	5.0(2)
C(12)	0.231(1)	0.3212(5)	0.1320(8)	4.0(2)
C(13)	0.208(1)	0.3069(5)	−0.0972(8)	3.6(2)
C(14)	0.297(1)	0.2458(4)	−0.0851(9)	3.3(2)
C(15)	0.220(1)	0.1896(5)	−0.1041(9)	3.5(2)
C(16)	0.306(1)	0.1333(6)	−0.0920(9)	4.3(2)
C(17)	0.461(1)	0.1341(4)	−0.0613(8)	4.4(2)
C(18)	0.535(1)	0.1894(6)	−0.047(1)	4.7(3)
C(19)	0.454(1)	0.2461(5)	−0.0566(8)	3.0(2)
N(1A)	0.4760(9)	0.9477(4)	0.1414(8)	4.1(2)
O(1A)	0.5973(8)	0.9540(6)	0.2013(7)	7.9(3)
O(2A)	0.3570(8)	0.9716(4)	0.1721(8)	5.5(2)
O(3A)	0.4773(8)	0.9164(4)	0.0436(7)	5.0(2)
N(1B)	0.156(1)	0.7089(4)	0.8200(7)	3.9(2)
O(1B)	0.192(1)	0.7569(4)	0.7660(8)	6.5(2)
O(2B)	0.0622(9)	0.7106(4)	0.8987(7)	5.7(2)
O(3B)	0.220(1)	0.6569(4)	0.7977(7)	6.4(2)
N(1C)	0.9758(9)	0.0475(4)	0.3081(8)	4.1(2)
O(1C)	0.8534(8)	0.0236(4)	0.2683(8)	6.1(2)
O(2C)	0.9816(8)	0.0752(4)	0.4076(6)	5.6(2)
O(3C)	1.0910(8)	0.0446(4)	0.2465(7)	5.7(2)
N(1D)	0.043(1)	0.5512(4)	0.3164(7)	4.2(2)
O(1D)	−0.0873(9)	0.5285(4)	0.3071(8)	7.3(2)
O(2D)	0.1589(8)	0.5170(4)	0.3044(7)	4.9(2)
O(3D)	0.068(1)	0.6087(4)	0.3326(8)	6.1(2)
N(1E)	0.421(1)	0.9394(4)	0.7506(9)	4.9(2)
O(1E)	0.403(1)	0.9917(4)	0.7895(9)	7.8(3)
O(2E)	0.3148(9)	0.9001(4)	0.7572(8)	6.7(2)
O(3E)	0.536(1)	0.9261(6)	0.701(1)	10.6(3)
N(1F)	0.269(1)	0.7685(4)	0.2605(9)	4.4(2)
O(1F)	0.3451(9)	0.7381(4)	0.3385(7)	5.9(2)
O(2F)	0.168(1)	0.7444(5)	0.1907(8)	7.3(2)
O(3F)	0.290(1)	0.8260(4)	0.2533(8)	6.6(2)
O(91)	0.382(1)	0.9110(5)	0.4441(8)	7.0(2)
O(92)	0.1042(9)	0.5954(4)	0.0471(7)	5.3(2)
O(93)	0.457(1)	0.7881(4)	0.6386(8)	6.2(2)

Fractional coordinates.

Table 3. Selected Bond Distances (Å) of [Co(NH$_3$)$_4$(Been)](NO$_3$)$_3$·1.5H$_2$O

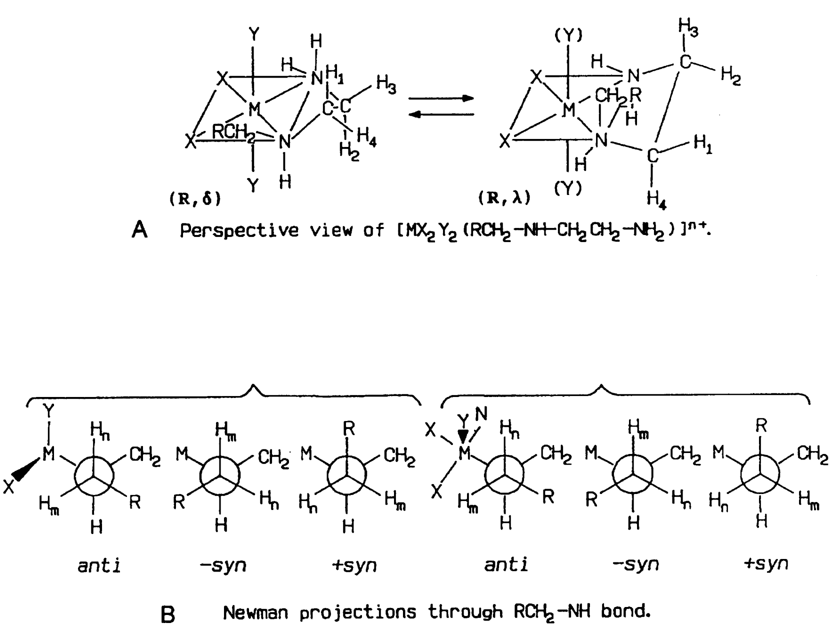
Molecule **1**		Molecule **2**	
Co(1)–N(1)	1.978(7)	Co(2)–N(11)	1.945(6)
Co(1)–N(2)	2.016(7)	Co(2)–N(12)	1.998(8)
Co(1)–N(3)	1.967(6)	Co(2)–N(13)	1.966(7)
Co(1)–N(4)	1.974(8)	Co(2)–N(14)	1.960(7)
Co(1)–N(5)	1.969(7)	Co(2)–N(15)	1.992(8)
Co(1)–N(6)	1.952(7)	Co(2)–N(16)	1.975(8)
N(1)–C(1)	1.50(1)	N(11)–C(11)	1.47(1)
N(2)–C(2)	1.472(9)	N(12)–C(12)	1.46(1)
N(2)–C(3)	1.48(1)	N(12)–C(13)	1.46(1)
C(1)–C(2)	1.48(1)	C(11)–C(12)	1.48(1)
C(3)–C(4)	1.51(1)	C(13)–C(14)	1.51(1)
C(4)–C(5)	1.36(1)	C(14)–C(15)	1.38(1)
C(4)–C(9)	1.41(1)	C(14)–C(19)	1.36(2)
C(5)–C(6)	1.37(1)	C(15)–C(16)	1.41(2)
C(6)–C(7)	1.39(1)	C(16)–C(17)	1.36(1)
C(7)–C(8)	1.36(1)	C(17)–C(18)	1.34(2)
C(8)–C(9)	1.37(1)	C(18)–C(19)	1.39(2)

Table 4. Bond Angles (°) of [Co(NH$_3$)$_4$(Been)]-(NO$_3$)$_3$·1.5H$_2$O

Molecule **1**		Molecule **2**	
N(1)–Co(1)–N(2)	86.2(3)	N(11)–Co(2)–N(12)	85.7(3)
N(1)–Co(1)–N(3)	178.7(3)	N(11)–Co(2)–N(13)	178.7(3)
N(1)–Co(1)–N(4)	88.7(3)	N(11)–Co(2)–N(14)	90.6(3)
N(1)–Co(1)–N(5)	91.8(4)	N(11)–Co(2)–N(15)	91.2(3)
N(1)–Co(1)–N(6)	90.0(3)	N(11)–Co(2)–N(16)	90.3(3)
N(2)–Co(1)–N(3)	94.9(3)	N(12)–Co(2)–N(13)	93.4(3)
N(2)–Co(1)–N(4)	174.8(2)	N(12)–Co(2)–N(14)	175.5(4)
N(2)–Co(1)–N(5)	89.4(3)	N(12)–Co(2)–N(15)	92.9(3)
N(2)–Co(1)–N(6)	92.2(2)	N(12)–Co(2)–N(16)	88.1(4)
N(3)–Co(1)–N(4)	90.3(3)	N(13)–Co(2)–N(14)	90.3(4)
N(3)–Co(1)–N(5)	87.5(3)	N(13)–Co(2)–N(15)	89.8(3)
N(3)–Co(1)–N(6)	90.7(3)	N(13)–Co(2)–N(16)	88.7(3)
N(4)–Co(1)–N(5)	90.6(3)	N(14)–Co(2)–N(15)	89.5(3)
N(4)–Co(1)–N(6)	87.9(3)	N(14)–Co(2)–N(16)	89.5(3)
N(5)–Co(1)–N(6)	177.7(3)	N(15)–Co(2)–N(16)	178.3(3)
Co(1)–N(1)–C(1)	109.1(5)	Co(2)–N(11)–C(11)	112.1(5)
Co(1)–N(2)–C(2)	106.0(5)	Co(2)–N(12)–C(12)	107.5(6)
Co(1)–N(2)–C(3)	118.1(5)	Co(2)–N(12)–C(13)	121.7(6)
C(2)–N(2)–C(3)	113.3(6)	C(12)–N(12)–C(13)	118.8(8)
N(1)–C(1)–C(2)	108.0(6)	N(11)–C(11)–C(12)	111.3(7)
N(2)–C(2)–C(1)	110.2(7)	N(12)–C(12)–C(11)	111.9(7)
N(2)–C(3)–C(4)	113.1(8)	N(12)–C(13)–C(14)	114.2(8)
C(3)–C(4)–C(5)	122(1)	C(13)–C(14)–C(15)	119.5(9)
C(3)–C(4)–C(9)	120.5(9)	C(13)–C(14)–C(19)	120.4(9)
C(5)–C(4)–C(9)	117.9(9)	C(15)–C(14)–C(19)	120(1)
C(4)–C(5)–C(6)	123(1)	C(14)–C(15)–C(16)	118(1)
C(5)–C(6)–C(7)	120(1)	C(15)–C(16)–C(17)	121(1)
C(6)–C(7)–C(8)	118(1)	C(16)–C(17)–C(18)	119(1)
C(7)–C(8)–C(9)	122.9(9)	C(17)–C(18)–C(19)	121(1)
C(4)–C(9)–C(8)	119.0(9)	C(14)–C(19)–C(18)	120(1)

of 1,2-diamine complexes of these transition metal ion complexes,[13] but both the Been complexes show strong absorptions in the ultraviolet region due to the phenyl ring.

The methylene region of the 400 MHz ^{1}H NMR spec-



A Perspective view of $[MX_2Y_2(RCH_2-NH-CH_2CH_2-NH_2)]^{n+}$.

B Newman projections through RCH_2-NH bond.

Fig. 1. Stereochemical scheme of coordinated *N*-alkylethanediamine.

tra of $[Co(CN)_4(Eten)]^-$ in 0.03 M NaOD–D_2O (N–D conditions) and in D_2O (N–H conditions) are reproduced in Figs. 2 and 3, respectively.[14)] A pair of apparent sextets at 3.23 and 2.87 ppm under N–D conditions was reduced to an AB quartet on irradiation at the methyl region (1.24 ppm) of the *N*-ethyl group. These signals were, therefore, assigned to H_m and H_n with ^2J of −13.6 Hz. Moreover, each peak split into a doublet by coupling with H_1: $^4J_{HCNCH}$ of 1.2 and 0.5 Hz were observed for the signals at 3.23 and 2.87 ppm, respectively. Under the NH conditions, H_m and H_n signal splits into a double doublet by coupling with N*H*, as shown in Fig. 3. The upfield and downfield signals have $^3J_{HCNH}$ of 9.8 and ca. 2 Hz, respectively. The difference in $^3J_{HCNH}$ can be accounted for by either the *anti* or the *syn* conformations, but the difference in $^4J_{HCNCH}$ suggests that the proton which appeared at lower field has a larger coupling constant than that which appeared at higher field. These differences indicate the predominant population of the anti conformation for the *N*-ethyl group in Fig. 1B. A LAOCN simulation[15)] assuming a 4 spin system for the ethane segment of ethanediamine has led to values of chemical shifts and coupling constants similar to those for $[Co(CN)_4(Meen)]^-$.[3b)]

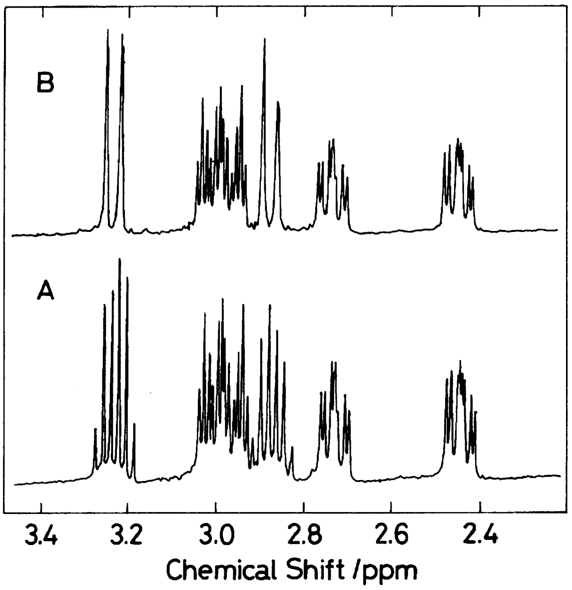


Fig. 2. Methylene region of 400 MHz ^1H NMR spectra of $[Co(CN)_4(Eten)]^-$ under N–D conditions. A, non irradiated, B, irradiated at methyl signal.

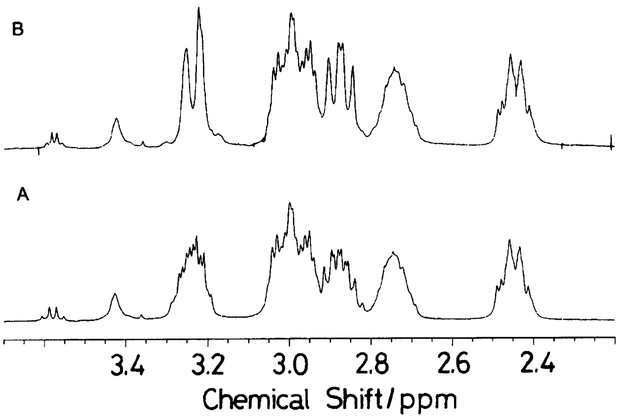


Fig. 3. Methylene region of 400 MHz ^1H NMR spectra of $[Co(CN)_4(Eten)]^-$ under N–H conditions. A, non irradiated; B, irradiated at methyl signal.

The methylene regions of the 400 MHz ^1H NMR spectra of $[Co(CN)_4(Been)]^-$ in D_2O (N–H conditions) and 0.03 M NaOD–D_2O (N–D conditions) are reproduced in Fig. 4. The benzyl protons, H_m and H_n, appeared as an AB quartet under the N–D conditions. The up-

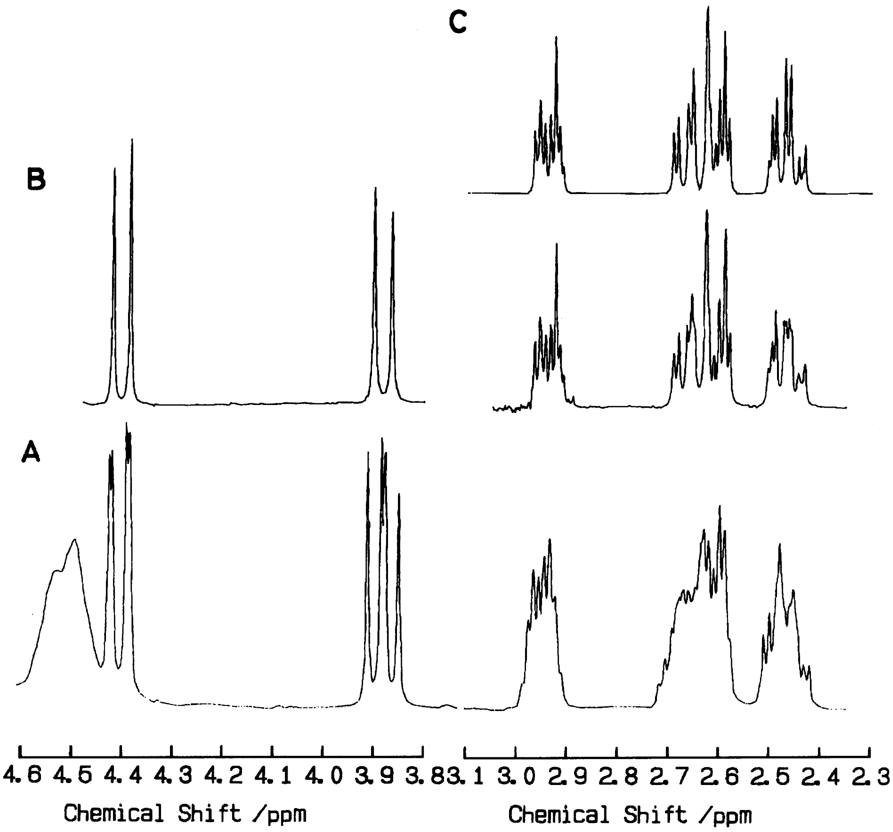


Fig. 4. Benzyl (4.6—3.8 ppm) and methylene (3.1—2.3 ppm) of 400 MHz ^1H NMR spectra of $[Co(CN)_4(Been)]^-$: A, under N–H conditions; B, under N–D conditions; C, simulated spectrum for the methylene region by LAOCN.

field and lowfield signals appeared as a triplet and a doublet under N–H conditions. The $^3J_{HCNH}$ of benzyl protons (H_n and H_m) were 10.7 and about 2 Hz respectively. Thus the conformation of the benzyl group takes a particular preferred conformation. This is supported by the analysis of the ethane segment of ethanediamine of the five-membered chelate ring. The four protons of the ethane segment of ethanediamine resonate as two groups: one single proton resonate at lower field and three protons resonate at a higher field. The simulation showed that the equatorial proton, H_4, resonated at the field higher by 0.6 ppm than the equivalent proton of $[Co(CN)_4(Eten)]^-$. This upfield shift must be caused by the presence of the phenyl group. If the phenyl group takes the anti conformation, the phenyl group will take a position near to H_4 in the chelate ring with fixed conformation.

The methylene region of the ^1H NMR spectrum of $[Co(NH_3)_4(Eten)]^{3+}$ and its simulated spectrum are reproduced in Fig. 5. The irradiation at the methyl signal reduced the multiplets of CH_2 of *N*-ethyl group to an AB quartet. The spectrum is rather complicated, but the values listed in Table 5 gave the satisfactory simulated spectrum shown in Fig. 5(B). Thus H_m and H_n resonated at different magnetic fields, though the difference in chemical shift was small (0.071 ppm) compared to that of tetracyano chelate.

The 400 MHz ^1H NMR spectrum of a D_2O solution of $[Co(NH_3)_4(Been)]^{3+}$ is shown in Fig. 6, along with the simulation trace of the ethane segment. The chemical shift and coupling constants are listed in Table 5. One of the equatorial chelate ring protons shifts upfield as the corresponding tetracyano complexes. The LAOCN simulation shows that the upfield shifted proton is H_4. The benzyl methylene resonated at 3.99 and 3.57 ppm.

The results of ^1H NMR measurements of DMSO solutions of $[Co(NH_3)_4(Eten)]^{3+}$ and $[Co(NH_3)_4(Been)]^{3+}$ are also listed in Table 5. The methylene protons of the Eten complex appear as a quartet and the difference in chemical shift between the two benzyl protons decreased compared with that in D_2O solution. Solvents influence the rotational barrier of $N–CH_2$ bond. A plausible cause is the difference in ability of formation of the hydrogen bond for N–H and for the solvents.

The entire signal pattern for the Fe(II) complex, $[Fe(CN)_4(Eten)]^{2-}$, is similar to that for the corresponding Co(III) complex. Irradiation at the methyl signal reduced the H_m and H_n signals to an AB quartet with ^2J of −13.3 Hz, which is close to that for the Co(III) complex. The couplings of H_m and H_n with NH observed under NH conditions were also similar as the corresponding Co(III) complex. The ethyl group of the Fe(II) complex therefore takes an anti conformation predominately.

The ^1H NMR spectrum of the $[Fe(CN)_4(Eten)]^-$ is shown in Fig. 7. The ^1H resonances of H_2, H_1, $C\underline{H}_3$, H_4,

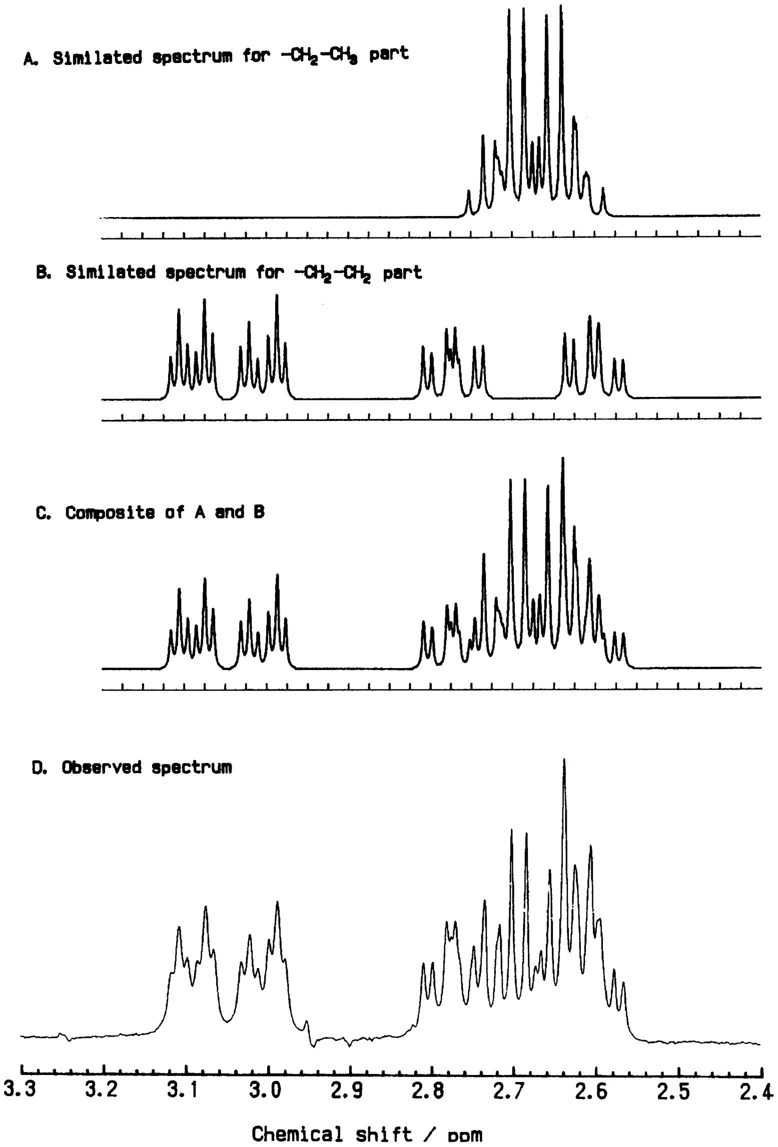


Fig. 5. Methylene region of 400 MHz ^{1}H NMR spectrum of $[Co(NH_3)_4(Eten)]^{3+}$ in D_2O (A) and its simulated spectrum for CH_2–CH_3 and ethane segment.

Table 5. Chemical Shifts and Coupling Constants for the Ethylenediamine Segment of $[M(L_2)_4(L_1)]^{n+}$ in D_2O

M	L_1	L_2	δ_1	δ_2	δ_3	δ_4	J_{12}	J_{13}	J_{14}	J_{23}	J_{24}	J_{34}	δ_m	δ_n	J_{mn}	J_{Me}	δ_R
Co	Eten	CN	2.44	2.73	2.85	3.01	10.1	4.3	−12.2	−12.9	4.1	4.9	3.23	2.83	−13.6	7.2	1.24
Co	Eten	NH_3	2.60	2.77	3.00	3.08	11.7	4.5	−13.6	−12.6	4.4	4.0	2.71	2.63	−12.9	7.1	1.35
Fe	Eten	CN	2.09	2.43	2.75	2.75	9.1	3.6	−13.4	−13.1	4.0	3.9	3.09	2.65	−13.3	7.1	1.15
Co	Been	CN	2.44	2.65	2.93	2.58	10.6	3.9	−12.2	−12.7	3.9	4.0	4.37	3.85	−13.8		
Co	Been	NH_3	2.61	2.67	2.95	2.56	12.1	4.6	−10.0	−10.8	4.5	2.4	3.99	3.57	−13.0		
Co	Meen	CN[a]	2.46	2.69	2.93	2.96	10.5	4.7	−13.3	−13.1	4.5	4.0					
Co	Meen	NH_3 [a]	2.67	2.77	2.94	2.96	12.2	4.6	−13.1	−13.2	4.6	2.5					

Chemical Shifts of DMSO Solution

	NH_3	NH_2 or NH	CH_2(ethanediamine)	CH_2	CH_3
Co Eten NH_3	3.61, 3.31, 3.22, 3.19	5.08, 5.03, 4.88	2.78, 2.74, 2.56, 2.46	2.47	1.20
Co Been NH_3	3.86, 3.65, 3.40, 3.39	5.33, 5.16, 4.97	2.70, 2.52, 2.42, 2.19	3.70, 3.50	

a) Ref. 3b.

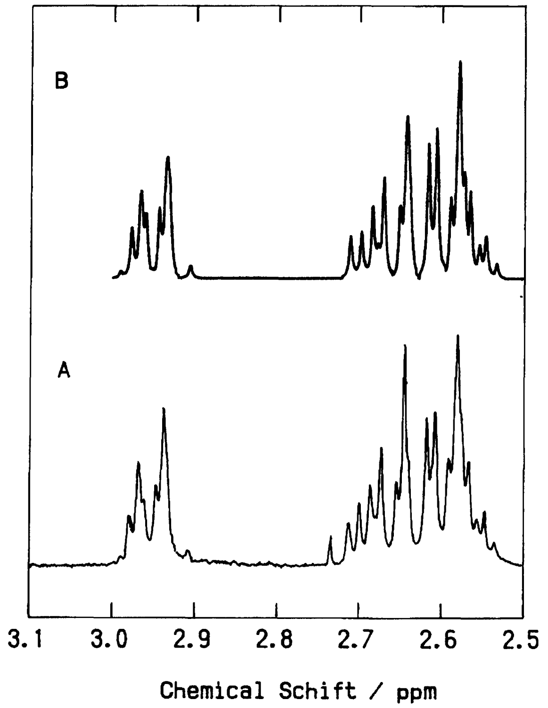


Fig. 6. Methylene region of 400 MHz ^1H NMR spectrum of $[Co(NH_3)_4(Been)]^{3+}$ in D_2O. A, observed. B, simulated by the data listed in Table 5.

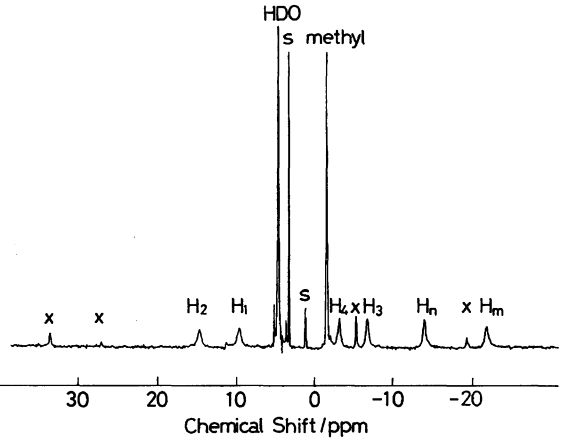


Fig. 7. ^1H NMR spectrum of $[Fe(CN)_4(Eten)]^-$ generated in situ by oxidation of the corresponding Fe(II) complex with $Na_2S_2O_8$ in 0.01 M DCl. s, solvent (methanol or ethanol); x, probably due to the tetracyanoferrate(III) of dehydrogenated Eten.

H_3, H_m, and H_n appeared at 14.69, 9.63, −1.61, −3.20, −6.86, −14.02, and −21.79 ppm with an area ratio of 1 : 1 : 3 : 1 : 1 : 1 : 1, respectively. The assignment was carried out based on the linear relation between the time-averaged chemical shift and the mole fraction of the Fe(III) complex for the mixture of the Fe(III) and Fe(II) complexes,[16] prepared by adding known amounts of $K_3[Fe(CN)_6]$ to $[Fe(CN)_4(Eten)]^{2-}$. The large difference in chemical shift between H_2 and H_3 shows that these protons locate mainly at axial and equatorial position, but the difference between H_1 and H_4 is small. The large difference in chemical shift of 7.77 ppm between H_m and H_n shows that these protons are located in different environments. The CH_3 resonance was found at −1.61 ppm, while $[Fe(CN)_4(N,N'\text{-dimethylethanediamine})]^-$ resonated at −17.4 ppm.[17]

To confirm the structure of $[Co(NH_3)_4(Been)]^{3+}$, the crystal structure of $[Co(NH_3)_4(Been)](NO_3)_3\cdot1.5H_2O$ has been determined. The monoclinic crystal contained two independent stereoisomers of the Co complex ions, **1** and **2**. The benzylethanediamine is coordinated as a bidentate ligand to the cobalt(III), which forms a regular octahedral structure. ORTEP drawings of the two complex cations are shown in Fig. 8; they are almost mirror images of each other, but are different in the rotation angles about the C(3)–C(4) axis. The distances between Co and the primary amine nitrogens are 1.978(7) and 1.945(6) Å, while those between Co and secondary amine nitrogen atoms are 2.016(7) and 1.998(8) Å. The distances between Co and the ammine nitrogens are in the range between 1.952(7) and 1.992(8) Å. The bite angles of N(1)–Co–N(2) are 86.2(3) and 85.7(3)° for cations **1** and **2**, respectively. On the other hand, the bond angles of the N(2)–Co–N(3), where the benzyl substituent extends, are widened to 94.9 and 93.4°. The presence of the substituent causes a slight widening of the bond angles around N(2): N(6)–Co–N(2), 92.2° for **1** and N(5)–Co–N(2), 92.2° for **2**. The bond angles of Co–N(2)–C(3) are close to 120° : 118.1(5)° and 121.7(6)° for **1** and **2**, respectively, while the Co–N(2)–C(2) take angles narrower than the tetrahedral value: 106.0(5) and 107.5(6) for **1** and **2**, while the remaining C(2)–N(2)–C(3) angles have intermediate angles: 113.3(6) and 118.8(8)°.

The planes of the phenyl rings tilted by 23.6° and 15.9° from the plane defined by four nitrogen atoms, consequently the ethane segments extend from N(2) to N(1), in the direction nearly perpendicular to the phenyl ring plane. The Co–N(2)–C(3)–C(4) torsion angles are 178.7(6) and −178.7(6)°; thus the benzyl groups take anti conformation, as was drawn in Fig. 1. The two benzyl hydrogens (H(8) and H(9)) have equivalent positions with respect to the phenyl ring, but H(8) of **1** and H(29) of **2** have characteristics of anti to the N–H hydrogens of the secondary amine and axial with respect to the five-membered chelate ring. Thus the two hydrogens resonate in different magnetic fields and the upper field protons have a large coupling constant with the N–H protons. The torsion angles for N(1)–C(1)–C(2)–C(3) are 50.4(8)° and −35(1)° for **1** and **2**, respectively.

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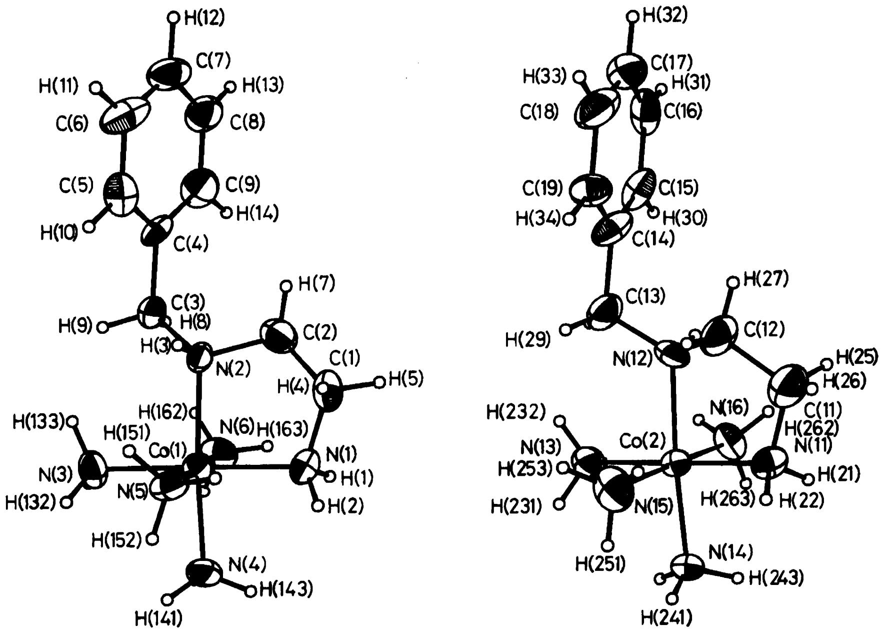

Fig. 8. ORTEP drawing of crystallographically independent complex cations.

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