RESEARCH ARTICLES

MACROBICYCLIC COBALT(III) HEXAAMINE COMPLEXES BASED ON TRIS(PROPYLENEDIAMINE) COBALT(III)

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ABSTRACT

The cage complexes : Δ,fac-lel$_3$-[Co (NO$_2$)$_2$Me$_3$sar]$^{3+}$ (1) (where (NO$_2$)$_2$Me$_3$ sar = 1, 8-dinitro-(4R, 12R, 17R)-trimethyl-3, 6, 10, 13, 16, 19-hexaazabicyclo [6.6.6] eicosane) and Δ, fac-lel$_3$-[Co(Me$_3$sep)]$^{3+}$ (3) (where (Me$_3$sep) = (4R, 12R, 17R)-trimethyl-1, 3, 6, 8, 10, 13, 16, 19-octaazabicyclo [6.6.6] eicosane) and their corresponding halfcage complexes : Δ, fac-lel$_3$-[Co(NO$_2$, Me$_3$semisar)]$^{3+}$ (2) (where (NO$_2$Me$_3$semisar) = tris(((2-aminopropyl) amino) methyl)nitromethane) and Δ, fac-lel$_3$-[Co(Me$_3$semisep)]$^{3+}$ (4) (where (Me$_3$semisep) = tris(((2-aminopropyl) amino) methyl)amine) are synthesized from Δ, fac-lel$_3$-[Co (R)(-)pn $_3$]$^{3+}$. Likewise their Λ-enantiomers are synthesised from Λ, fac-lel$_3$-[Co (S)(+)pn $_3$]$^{3+}$. The specific rotations, infrared spectra, visible spectra, nuclear magnetic resonance spectra and oxidation-reduction potentials are recorded.

INTRODUCTION

A range of macrobicyclic cobalt(III) hexaamine complexes based on tris(ethylenediamine) cobalt(III) ion ([Co(en)$_3$]$^{3+}$) have been known for over a decade[1, 2, 3, 4]. Among these complexes, [Co(dinosar)]$^{3+}$ and [Co(sep)]$^{3+}$ are most readily synthesised[4, 5] (dinosar = 1, 8-dinitro-3, 6, 10, 13, 16, 19-hexaazabicyclo[6.6.6] icosane and sep or sepulchrate = 1, 3, 6, 8, 10, 13, 16, 19-octaazabicyclo[6.6.6] icosane). Tris(R*-propylenediamine) cobalt(III) ions are one of the earliest tris-chelate complex ions that have been successfully prepared[6, 7]. Unlike symmetrical ethylenediamine, propylenediamine is unsymmetrical and optically active. Hence [Co($\pm$)pn$_3$]$^{3+}$. exist in twenty-four isomers and almost all of which have already been isolated and identified[8]. [Co($\pm$)pn$_3$]$^{3+}$ ions, considering their structures, can be regarded as trimethyl-substituted derivatives of tris(ethylenediamine) cobalt(III) ion. Therefore similar

macrobicyclic cobalt(III) hexaamine complexes based on tris(R^*-propylenediamine) cobalt(III) ions are expected to be successfully prepared by similar organic template reactions. In this work we are reporting only the syntheses of the analogs of $[Co(dinosar)]^{3+}$ and $[Co(sep)]^{3+}$

Among the twenty-four isomers of $[Co(\pm)pn_3]^{3+}$, it has been found that $\Lambda[Co(S)(+)pn_3]^{3+}$ and $\Delta[Co(R)(-)pn_3]^{3+}$ are the most stable and the first fraction to be isolated by the method of either fractional crystallisation[6] or cellulose column chromatography[7, 8]. However $\Lambda[Co(S)(+)pn_3]^{3+}$ and $\Delta[Co(R)(-)pn_3]^{3+}$ may exist in two geometrical isomeric forms : fac- (5) and mer- (6) Nevertheless it has been proven by X-ray crystallography that the stable crystalline $\Lambda[Co(S)(+)pn_3]^{3+}$ and $\Delta[Co(R)(-)pn_3]^{3+}$ are in the fac-form and have lel_3 conformation[9, 10, 11]. Therefore the syntheses of the analogs of $[Co(dinosar)]^{3+}$ and $[Co(sep)]^{3+}$ are the attempt to encapsulate Λ, fac-lel_3-$[Co(S)(+)pn_3]^{3+}$ and Δ, fac-lel_3-$[Co(R)(-)pn_3]^{3+}$.

Examining the structure of Δ, fac-lel_3-$[Co(R)(-)pn_3]^{3+}$, it is obvious that all three methyl groups are on the same side of the plane perpendicular to C_3 axis, causing a strong steric hindrance on that side. It is expected that the less hindered side of the trischelate is capped first, almost as a facile as in the case of $[Co(en)_3]^{3+}$, then the cage is slowly completed on the most hindered side. This stepwise mechanism is supported by the success in isolating the halfcage complexes.

For simplicity, the following abbreviations are adopted[12] :

Δ, fac-lel_3-$[Co(NO_2)_2Me_3sar]^{3+}$	=	the analog of $[Co(dinosar)]^{3+}$ based on Δ, fac-lel_3-$[Co(R)(-)pn_3]^{3+}$
Δ, fac-lel_3-$[Co(Me_3sep)]^{3+}$	=	the analog of $[Co(sep)]^{3+}$ based on Δ, fac-lel_3-$[Co(R)(-)pn_3]^{3+}$
Δ, fac-lel_3-$[Co(NO_2, Me_3semisar)]^{3+}$	=	the halfcage analog of $[Co(dinosar)]^{3+}$ based on Δ, fac-lel_3-$[Co(R)(-)pn_3]^{3+}$
Δ, fac-lel_3-$[Co(Me_3semisep)]^{3+}$	=	the halfcage analog of $[Co(sep)]^{3+}$ based on Δ, fac-lel_3-$[Co(R)(-)pn_3]^{3+}$.

Note that the successful syntheses of Δ, Λ, fac-lel_3-$[Co(NO_2)_2Me_3sar]^{3+}$ had already been mentioned but with neither the detailed preparations nor the indication of the existance of the corresponding halfcage complexes[12] given.

MATERIALS AND METHODS

Infrared Spectra were recorded with a Jasco Model A-302 IR Spectrophotometer. Electronic Spectra were recorded with a Shimadzu UV-240 Spectrophotometer. ^{1}H NMR Spectra were recorded with a Varian Model EM 360A 60 MHz. instrument. Optical rotation data were measured with a CARL ZEISS 93662 Polarimeter. Elemental microanalyses were carried out with a Perkin-Elmer 2400 elemental analyser at the UNESCO Analytical Service Centre, Silpakorn University.

Structures

3+

1

3+

2

3+

3

3+

4

fac-

5

mer-
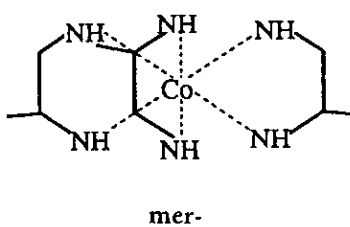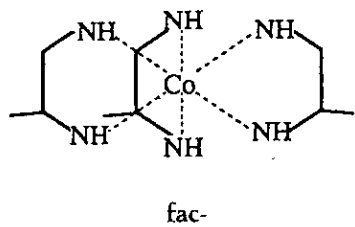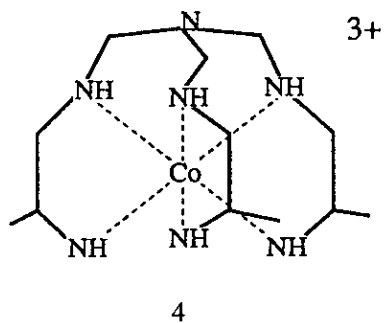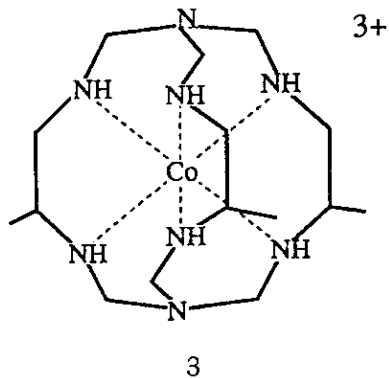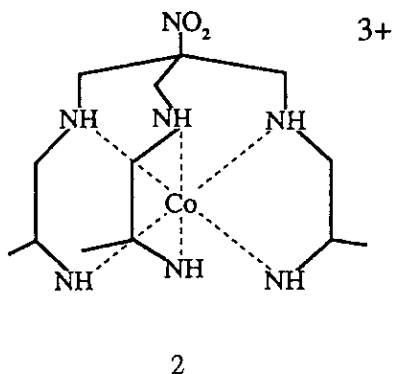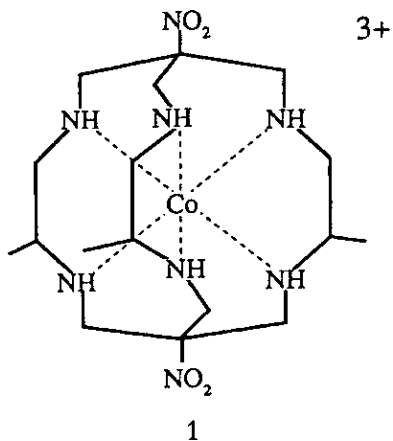
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Resolution of R*-Propylenediamine.[6]

(-)-Propylenediamine.

R*-propylenediamine (260 g, 325 ml) was added slowly with stirring to a solution of (+)-tartaric acid (700 g) in cold water (750 ml). The mixture, which had almost boiled, was allowed to cool slowly to 40°C and then cooled rapidly in ice to 5°C and kept overnight in a freezer. When thawed the crystalline diastereoisomer was filtered and washed with ice-water (250 ml). The filtrate was kept for later recovery of (+)-propylenediamine. The crude solid was then recrystallised from the minimum amount of boiling water and cooling at room temperature. The yield of air-dried white crystals of (-)-propylenediamine-(+)-tartrate was 466 g with $[\alpha]_D = 20°$.

(-)-propylenediamine-(+)-tartrate (466 g) was then reacted with 33% NaOH (300 ml), and solid NaOH (100 g) was added and mixed well. Then the whole content was distilled until the temperature was 110°C or just before the appearance of some yellow oil. The yield of the distillate was 540 ml and the concentration of (-)-propylenediamine in the distillate was determined by titration with HCl (0.1 M) to the methyl orange end-point (1.63 M).

(+)-Propylenediamine.

The filtrate after the separation of the crude (-)-propylenediamine-(+)-tartrate was evaporated on a rotary-evaporator to a volume of about 400 ml and solid NaOH (250 g) was added and stirred into the content. Then the crude solution of (+)-propylenediamine (3.74 M, 330 Ml) was recovered in exactly the same way as (-)-propylenediamine.

Synthesis of Δ, fac-lel$_3$-[Co(R)(-)pn$_3$]Br$_2$Cl.H$_2$O.[6, 7, 9, 11]

$CoCl_2.6H_2O$ (62.1 g), conc. HCl (52.6 ml) and (-)-propylenediamine solution (1.63 M, 535 ml) in water (153 ml) were oxidised in a stream of air in the presence of activated charcoal (26.5 g) for 12 hr. The solution was filtered and made slightly acid with HCl. The solution was evaporated to half of its initial volume on a rotary-evaporator and evaporated further on the steam-bath until a crust of solid was formed, then cooled and an equal volume of ethanol added. On standing in ice, crude yellow solid separated, then filtered and recrystallised from minimum amount of hot water. The yellow complex obtained was Δ, fac-lel$_3$-[Co(R)(-)pn$_3$]Cl$_3$, yield = 11.0 g.

Δ, fac-lel$_3$-[Co(R)(-)pn$_3$]Cl$_3$ (11.0 g) was then dissolved in hot water (50°C, 40 ml) and conc. HBr (40 ml) was added, then cooled in ice and the yellow-orange precipitate separated. The precipitate was filtered and recrystallised twice with the minimum amount of hot water. Slow cooling in the process of recrystallisation yielded yellow-orange, needle-like crystals (2.5 g). Anal. Calcd for CoCgH$_{32}$N$_6$Br$_2$ClO : Co, 11.91; C, 21.85; H, 6.52; N, 16.99. Found : Co, 11.97; C, 21.03; H, 6.01; N, 16.75.

$[\alpha]_D = -38°$ (cf. $[\alpha]_D$ of Δ, fac-lel$_3$-[Co(R)(-)pn$_3$]I$_3$ .H$_2$O = $-24°$[6, 7, 9, 11]).

Synthesis of Δ, fac-lel$_3$-[Co(NO$_2$, Me$_3$ semisar)]Br$_3$.H$_2$O.[4]

Δ, fac-lel$_3$-[Co(R)(-)pn$_3$]Br$_2$ Cl. H$_2$O (5.7 g) and anhydrous Na$_2$CO$_3$ (3.0 g) were dissolved in water (180 ml), then nitromethane (10 ml) and 37% aqueous formaldehyde (80 ml) were slowly added with constant stirring. The solution was kept at 40°C for 2 hr. The precipitate was filtered with suction then dissolved in conc. HBr (10 ml.) and yellow-orange precipitate separated when cooled in ice. The precipitate was recrystallised twice with the minimum amount of hot water and yielded orange crystals (0.4 g). Anal. calcd for CoC$_{13}$H$_{35}$N$_7$Br$_3$O$_3$: Co, 9.26; C, 24.54; H, 5.55; N, 15.41. Found : Co, 9.35; C, 23.56; H, 5.36; N, 15.22. $[\alpha]_D = 140°$.

Synthesis of Δ, fac-lel$_3$-[Co (NO$_2$)$_2$Me$_3$sar)Br$_3$.H$_2$O.

a. From Δ, fac-lel$_3$-[Co(NO$_2$, Me$_3$semisar)]Br$_3$.H$_2$O.

Δ, fac-lel$_3$-[Co(NO$_2$, Me$_3$ semisar)]Br$_3$.H$_2$O (0.6 g) was dissolved in water (14.7 ml), then nitromethane (0.9 ml) and 37% aqueous formaldehyde (7.5 ml) were added slowly with stirring and the solution was made alkaline with NaOH solution (0.1 M). The solution was kept at 40°C for 7 hr. Anhydrous Na$_2$CO$_3$ (0.3 g) was added with stirring until all dissolved and the solution was left standing at 40°C for further 2 hr. The precipitate was filtered with suction, then dissolved in the minimum amount of conc. HBr. When further addition of HBr gave no more liberation of CO$_2$, the solution was cooled in ice. After twice recrystallisations with the minimum amount of boiling water, Δ, fac-lel$_3$-[Co (NO$_2$)$_2$Me$_3$sar]Br$_3$.H$_2$O separated in the form of yellow powder (0.3 g). Anal.Calcd for CoC$_{17}$H$_{38}$N$_8$Br$_3$O$_5$: Co, 8.04; C, 27.85; H, 5.22; N, 15.28. Found : Co, 8.13; C, 27.35; H, 5.33; N, 14.86 $[\alpha]_D = 308°$.

b. From Δ, fac-lel$_3$-[Co(R)(-)pn$_3$] Br$_2$C1.H$_2$O.

Δ, fac-lel$_3$-[Co(R)(-)pn$_3$]Br$_2$ Cl. H$_2$O (5.7 g) was dissolved in water (360 ml), then nitromethane (20 ml) and 37% aqueous formaldehyde (160 ml) were added slowly with stirring and the solution was made alkaline with NaOH solution (0.1 M). The solution was kept in a thermostatted-bath at 40°C for 7 hr. Anhydrous Na$_2$CO$_3$ (6.0 g) was added with stirring until all dissolved and the solution was left standing at 40°C for 2 hr. The precipitate was filterd with suction, then dissolved in the minimum amount of HBr and cooled in ice. After twice recrystallisations with the minimum amount of boiling water, Δ, fac-lel$_3$-[Co (NO$_2$)$_2$Me$_3$sar]Br$_3$.H$_2$O separated in the form of yellow powder (0.5 g). Anal. Calcd for CoC$_{17}$H$_{38}$N$_8$Br$_3$O$_5$: Co, 8.04; C, 27.85; H, 5.22; N, 15.28. Found : Co, 8.02; C, 27.49; H, 5.76; N, 14.60. $[\alpha]_D = 308°$.

Synthesis of Δ, fac-lel$_3$-[Co(Me$_3$semisep)]Br$_3$.H$_2$O.[2]

To a stirred suspension of Δ, fac-lel$_3$-[Co(R)(-)pn$_3$]Br$_2$Cl.H$_2$O (12.5 g) and Li$_2$CO$_3$ (12.3 g) in water (63 ml) were added 27% aqueous ammonia (83 ml) diluted to 296 ml and 37% aqueous formaldehyde (296 ml). The solutions were added separately and continuously

over 2 hr by using a peristaltic pump. The mixture was stirred for another hour, then Li_2CO_3 filtered off, and the pH of the filtrate adjusted to ~ 3 with conc. $HClO_4$. The solution was cooled for ~ 3 hr in a freezer, then the white shiny solid formed was filtered off. The filtrate was adsorbed on an ion-exchange column (Dowex 50W-X2, 200-400 mesh, H^+ form, 2.5×10 cm). The column was eluted with trisodium citrate (0.2 M, 2 l) to remove a pink species, which was discarded. The resin bed was then washed with H_2O and HCl (1 M, 500 ml) to remove Na^+ and the orange species removed from the column by eluting with HBr (3 M, 1.5 l). The eluate was taken down to dryness on a rotary evaporator at 50°C. The isolated compound was dissolved in minimum amount of hot water (90°C) and made neutral with NaOH solution (0.1 M). On standing at room temperature, a yellow-orange precipitate separated. Recrystallisation from the minimum amount of hot water by slow cooling yielded yellow-orange, needle-like crystals (0.8 g). Anal. Calcd for $CoC_{12}N_7H_{35}Br_3O$: Co, 9.95; C, 24.34; H, 5.96; N, 16.56. Found : Co, 10.01; C, 24.04; H, 6.12; N, 16.41. $[\alpha]_D = -25°$.

Synthesis of Δ, fac-lel$_3$-[Co(Me$_3$sep)]Br$_3$.[2,5]

To a stirred suspension of Δ, fac-lel$_3$-[Co(R)(-)pn$_3$]Br$_2$Cl.H$_2$O (12.5 g) and Li_2CO_3 (12.3 g) in water (63 ml) were added 27% aqueous ammonia (83 ml) diluted to 296 ml and 37% aqueous formaldehyde (296 ml). The solutions were added separately and continuously over 2 hr by using a peristaltic pump. The mixture was stirred for another hour, then Li_2CO_3 filtered off, and the pH of the filtrate adjusted to ~ 3 with conc. $HClO_4$. The solution was cooled for ~ 3 hr in a freezer, then the white shiny solid formed was filtered off. The filtrate was concentrated on a rotary evaporator to 60 ml and Li_2CO_3 (12.3 g) was added. Aqueous ammonia and aqueous formaldehyde with the same concentrations and amounts as before were added with the use of a peristaltic pump. The mixture was stirred for another 12 hr, then Li_2CO_3 was removed and pH adjusted to ~ 3. The solution was cooled for ~ 3 hr, then filtered. $Na[S_2CNEt_2].3H_2O$ (60 g) was added to the filtrate and the mixture stirred for further 1 hr. The resultant brown oil consisting of red Δ, fac-lel$_3$-[Co(Me$_3$sep)][S$_2$CNEt$_2$]$_3$ and green $Co(S_2CNEt_2)_3$ was filtered and washed with little water. The oil was dissolved in acetonitrile (70 ml) and filtered. Conc. HBr was added dropwise to the brown-green solution with stirring until all pale orange powder separated and the solution turned green. The mixture was warmed on a hot plate for 10 min, then cooled slowly. The orange precipitate was filtered and washed well with acetonitrile. Recrystallisation from the minimum amount of hot water yielded red-orange crystals (0.5 g). Anal. Calcd for $CoC_{15}N_8H_{36}Br_3$: Co, 9.40; C, 28.72; H, 5.79; N, 17.87. Found : Co, 9.45; C, 28.43; H, 6.48; N, 17.80. $[\alpha]_D = 40°$.

RESULTS AND DISCUSSION

Syntheses.

Δ, fac-lel$_3$-[Co(NO$_2$, Me$_3$semisar)]$^{3+}$ and Δ, fac-lel$_3$-[Co(Me$_3$semisep)]$^{3+}$ were synthesized from Δ, fac-lel$_3$-[Co(R)(-)pn$_3$]$^{3+}$ in exactly the same way as [Co(dinosar)]$^{3+}$[4] and [Co(sep)]$^{3+}$[2] from [Co(en)$_3$]$^{3+}$. As Co$_3^{2-}$ forms insoluble salt with Δ, fac-lel$_3$-[Co(NO$_2$, Me$_3$ semisar)]$^{3+}$, the absence of CO$_3^{2-}$ at the start of the reaction is essential in the synthesis of Δ, fac-lel$_3$-[Co (NO$_2$)$_2$Me$_3$sar]$^{3+}$, hence the solution was made alkaline with NaOH instead. The synthesis of Δ, fac-lel$_3$-[Co(Me$_3$semisep)]$^{3+}$ was as facile as Δ, fac-lel$_3$-[Co(NO$_2$,Me$_3$ semisar)]$^{3+}$ and [Co(sep)]$^{3+}$ but a large excess of reagents and longer time were required in the synthesis of Δ, fac-lel$_3$-[Co(Me$_3$sep)]$^{3+}$. Attempt to purify Δ, fac-lel$_3$-[Co(Me$_3$sep)]$^{3+}$ by the method of ion-exchange column[2] was a failure, so a more convenient and successful method was employed, involving sodium diethyldithiocarbamate which forms insoluble salt with Δ, fac-lel$_3$-[Co(Me$_3$sep)]$^{3+}$ and decomposes into other uncaged species to form acetonitrile soluble Co(S$_2$CNEt$_2$)$_3$. HBr decomposes free diethyldithiocarbamate ion and hence converts Δ, fac-lel$_3$-[Co(Me$_3$sep)](S$_2$CNEt$_2$)$_3$ to acetonitrile insoluble Δ, fac-lel$_3$-[Co(Me$_3$sep)]Br$_3$. Practically pure bromide salt is obtained by thorough washing with acetonitrile. Λ, fac-lel$_3$-[Co(S)(+) pn$_3$]Cl.H$_2$O and the Λ-enantiomers of the complexes discussed were synthesized similarly. To prepare Λ, fac-lel$_3$-[Co(S)(+)pn$_3$]Br$_2$Cl.H$_2$O, (+)-propylenediamine prepared at the start of this work could be used but yielded much less product in comparison with the yield of Δ, fac-lel$_3$-[Co(R)(-)pn$_3$]Br$_2$Cl.H$_2$O. However similar yield to Δ, fac-lel$_3$-[Co(R)(-)pn$_3$]Br$_2$ Cl.H$_2$O could be obtained by using (+)-propylenediamine recovered from crystalline (+)-propylenediamine-(-)-tartrate (ie. (-)-tartaric acid was used in the resolution). Each Λ-enantiomer has the same value of specific angle of rotation as the corresponding Δ-enantiomer but with opposite sign.

Spectra.

Infrared Spectra. (KBr disc spectra)

Spectra of each Δ, Λ-enantiomeric pair are identical. Δ, fac-lel$_3$-[Co(R)(-)pn$_3$]Br$_2$Cl. H$_2$O has NH stretching (3500 cm^{-1}), CH stretching (3050 cm^{-1}), NH bending (1590 cm^{-1}) and CH bending (1470 cm^{-1}). Δ, fac-lel$_3$-[Co(NO$_2$,Me$_3$semisar)]Br$_3$.H$_2$O has 2° NH stretching (3450 cm^{-1}) and bending (1620 cm^{-1}), CH stretching (2840 cm^{-1}) and strong absorbance of -NO$_2$ (1550 cm^{-1}) due to the cap. Δ, fac-lel$_3$-[Co (NO$_2$)$_2$Me$_3$sar] Br$_3$.H$_2$O has 2° NH stretching (3450 cm^{-1}) and bending (1620 cm^{-1}), CH stretching (2850 cm^{-1}) and strong absorbance of -NO$_2$ (1555 cm^{-1}) due to both caps, with the disappearance of all the 1° NH stretching and bending. Δ, fac-lel$_3$-[Co(Me$_3$semisep)]Br$_3$.H$_2$O has 2° NH stretching (3480 cm^{-1}) and bending (1625 cm^{-1}) and CH stretching (2840 cm^{-1}) due to the cap. Δ, fac-lel$_3$-[Co(Me$_3$sep)]Br$_3$ has 2° NH stretching (3500 cm^{-1}) and bending (1620 cm^{-1}) and CH stretching (2850 cm^{-1}) due to both caps, with the disappearance of all the 1° NH stretching and bending.

Visible Spectra.

Fig. 1. shows the visible spectra of Δ, fac-lel$_3$-[Co(R)(-)pn$_3$]$^{3+}$, Δ, fac-lel$_3$-[Co(NO$_2$, Me$_3$semisar)]$^{3+}$ and Δ, fac-lel$_3$-[Co (NO$_2$)$_2$Me$_3$sar]$^{3+}$. Each of the complexes shows two absorption maxima which is typical of an octahedral saturated CoN$_6^{3+}$ chromophore : Δ, fac-lel$_3$-[Co(R)(-)pn$_3$]$^{3+}$ at 338 nm (ϵ = 92 M^{-1}cm^{-1}) and 465 nm (ϵ = 99 M^{-1}cm^{-1}), Δ, fac-lel$_3$-[Co(NO$_2$,Me$_3$semisar)]$^{3+}$ at 340 nm (ϵ = 106 M^{-1}cm^{-1}) and 468 nm (ϵ = 116 M^{-1}cm^{-1}) and Δ, fac-lel$_3$-[CO (NO$_2$)$_2$Me$_3$sar]$^{3+}$ at 342 nm (ϵ = 130 M^{-1}cm^{-1}) and 477 nm (ϵ = 136 M^{-1}cm^{-1}). The band maxima shift to longer wavelengths as each cap was added on the tris-propylenediamine chelate. The shift is the same as in the case of tris-ethylenediamine chelate[4]. Δ, fac-lel$_3$-[Co(Me$_3$semisep)]$^{3+}$ has two absorption maxima at 340 nm (ϵ = 104 M^{-1}cm^{-1}) and 468 nm (ϵ = 102 M^{-1}cm^{-1}). Δ, fac-lel$_3$-[Co(Me$_3$sep)]$^{3+}$ has a shoulder at 342 nm (ϵ = 126 M^{-1}cm^{-1}) and a maximum at 477 nm (ϵ = 106 M^{-1}cm^{-1}) which is very similar to the visible spectrum of [Co(sep)]$^{3+}$ [1]. The Λ-enantiomers give identical visible spectra to the complexes discussed above.

Nuclear Magnetic Resonance Spectra.

The ^{1}H NMR spectrum of Δ, fac-lel$_3$-[Co(R)(-)pn$_3$]$^{3+}$ in D$_2$O shows a doublet at ~ 1.2 ppm corresponding to 9 protons, due to the methyl groups of propylenediamine and a complex AA'BB' pattern at ~ 2.6 ppm integrating for 21 protons, due to the propylenediamine 9 methylene protons and 12 amino protons. Δ, fac-lel$_3$-[Co(NO$_2$,Me$_3$semisar)]$^{3+}$ and Δ, fac-lel$_3$-[Co(Me$_3$ semisep)]$^{3+}$ have similar ^{1}H NMR spectra with a doublet at ~ 1.2 ppm corresponding to 9 protons, due to the methyl groups of propylenediamine; a complex AA'BB' pattern at ~ 2.6 ppm due to the propylenediamine 9 methylene protons and 9 amino protons and an AB doublet pair with J ~ 12 Hz, due to 6 methylene protons of the cap at ~ 3.2 ppm for Δ, fac-lel$_3$-[Co(NO$_2$,Me$_3$semisar)]$^{3+}$ and at ~ 3.7 ppm for Δ, fac-lel$_3$-[Co(Me$_3$semisep)]$^{3+}$. The integration on the complex AA'BB' pattern and the AB doublet pair indicates 24 protons. Δ, fac-lel$_3$-[Co (NO$_2$)$_2$Me$_3$sar]$^{3+}$ and Δ, fac-lel$_3$-[Co(Me$_3$sep)]$^{3+}$ have similar ^{1}H NMR spectra with a doublet at ~ 1.2 ppm corresponding to 9 protons, due to the methyl groups of propylenediamine; a complex AA'BB' pattern at ~ 2.7 ppm due to the propylenediamine 9 methylene protons and 6 amino protons and a complex pattern ascribed as the result of the superimposition of two AB doublet pairs with J ~ 12 Hz, due to 12 methylene protons of the caps at ~ 3.3 ppm for Δ, fac-lel$_3$-[Co (NO$_2$)$_2$Me$_3$sar]$^{3+}$ and at ~ 3.8 ppm for Δ, fac-lel$_3$-[Co(Me$_3$sep)]$^{3+}$. The integration on the complex AA'BB' pattern and the complex AB doublet pairs indicates 27 protons. The ^{1}H NMR spectra of the Λ-enantiomers are also identical with those discussed above.

Redox Properties.

All cyclic voltammetric measurements were carried out in 0.1 M NaClO$_4$; using Ag/AgCl in 1 M KCl as reference electrode, Pt electrodes as working electrode and auxilliary electrode. The reduction is reversible for all complexes except for Δ, fac-lel$_3$-[Co(R)(-)pn$_3$]$^{3+}$, Λ, fac-lel$_3$-[Co(S)(+)pn$_3$]$^{3+}$ and Δ, Λ, fac-lel$_3$-[Co(NO$_2$,Me$_3$semisar)]$^{3+}$. Similar results were obtained using
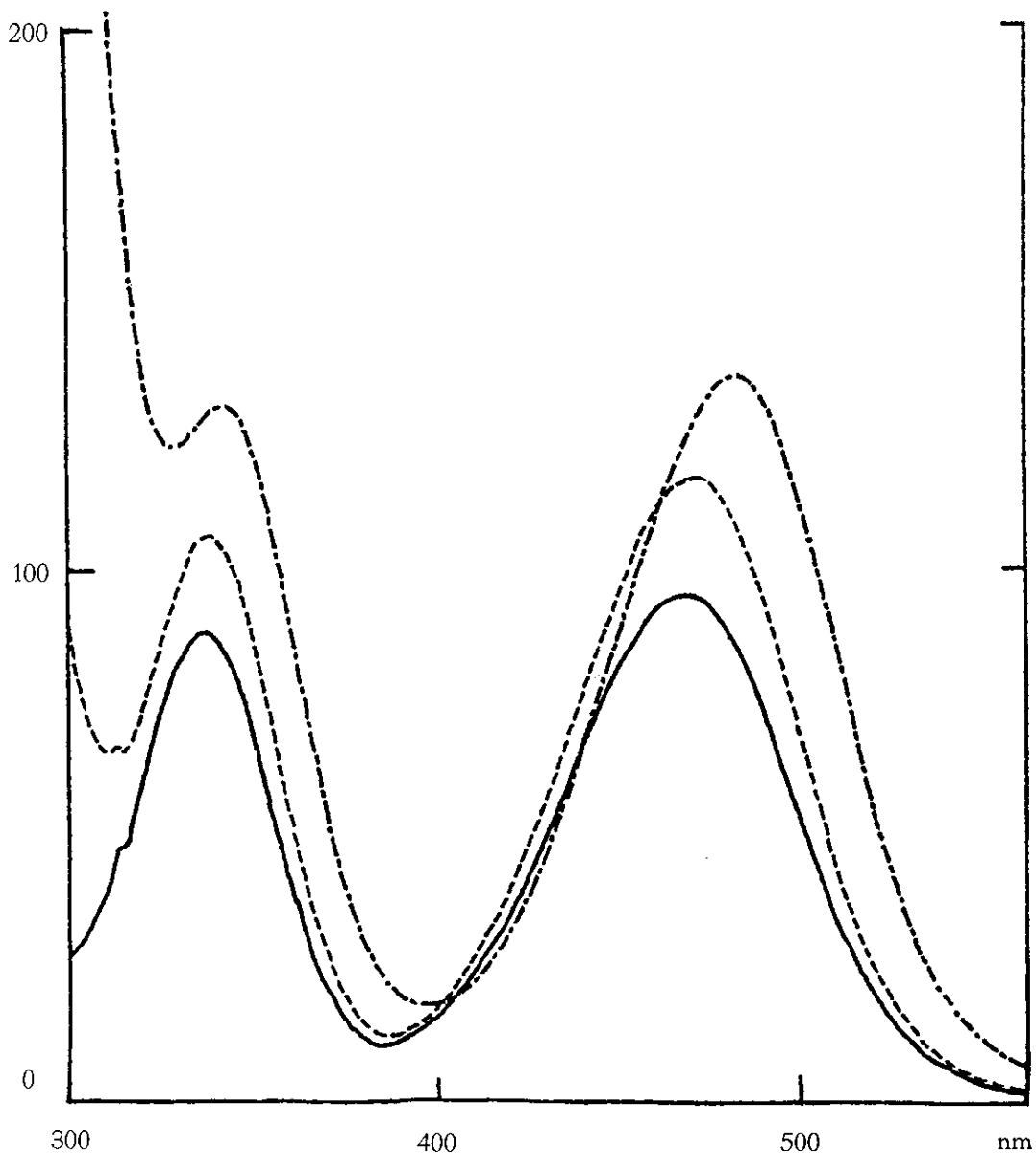
Fig. 1. Visible spectra of Δ, fac-lel$_3$-[Co(R)(-)pn$_3$]$^{3+}$ (_____),
Δ, fac-lel$_3$-[Co(NO$_2$,Me$_3$semisar)]$^{3+}$ (---), and
Δ, fac-lel$_3$-[Co (NO$_2$)$_2$Me$_3$sar]$^{3+}$ (-•-).

TABLE 1. Standard reduction potentials of the complexes in 0.1 M $NaClO_4$.

Complexes	E°/V
$[Co(en)_3]^{3+}$	-0.13[2]
$[Co(dinosar)]^{3+}$	$+0.04$[4]
$[Co(sep)]^{3+}$	-0.26[2]
Δ, fac-lel$_3$-[Co(R)(-)pn$_3$]$^{3+}$, Λ, fac-lel$_3$-[Co(S)(+)pn$_3$]$^{3+}$	-0.22[13]
Δ, Λ, fac-lel$_3$-[Co(NO$_2$,Me$_3$semisar)]$^{3+}$	-0.17
Δ, Λ, fac-lel$_3$-[Co (NO$_2$)$_2$Me$_3$sar]$^{3+}$	-0.02
Δ, Λ, fac-lel$_3$-[Co(Me$_3$semisep)]$^{3+}$	-0.28
Δ, Λ, fac-lel$_3$-[Co(Me$_3$sep)]$^{3+}$	-0.33

a rotating gold-disc electrode as working electrode. Taking $E°$ of Ag/AgCl in 1 M KCl to be 0.22 V, the values of $E°$ of all the complexes studied are calculated from their $E_{1/2}$ values and shown in Table 1., which also contains $E°$ values of $[Co(en)_3]^{3+}$, $[Co(dinosar)]^{3+}$ and $[Co(sep)]^{3+}$ from the literature. The reduction potential of Δ, Λ, fac-lel$_3$-[Co (NO$_2$)$_2$Me$_3$sar]$^{3+}$ is higher than that observed for Δ, Λ, fac-lel$_3$-[Co(NO$_2$,Me$_3$semisar)]$^{3+}$ which is in turn higher than that of $[Co(pn)_3]^{3+}$. On the contrary, $E°$ of Δ, Λ, fac-lel$_3$-[Co(Me$_3$sep)]$^{3+}$ is lower than $E°$ of Δ, Λ, fac-lel$_3$-[Co(Me$_3$semisep)]$^{3+}$ which is in turn lower than $E°$ of $[Co(pn)_3]^{3+}$. Similar trend is observed in the case of $[Co(dinosar)]^{3+}$ and $[Co(sep)]^{3+}$ with respect to $[Co(en)_3]^{3+}$. Comparing $E°$ of $[Co(pn)_3]^{3+}$ with that of $[Co(en)_3]^{3+}$, it is obvious that $[Co(pn)_3]^{3+}$ is harder to be reduced than $[Co(en)_3]^{3+}$, which seems to imply that methyl groups are hindrance to electron transfer. Similarly the caps of the sep and the Me$_3$sep ligands seem to hinder electron transfer. Whereas the caps of the dinosar and the (NO$_2$)$_2$Me$_3$sar ligands, with $-NO_2$ groups seem to conduct electrons. Apart from the reduction of cobalt(III) to cobalt(II), it was found that in the case of Δ, Λ, fac-lel$_3$-[Co(NO$_2$,Me$_3$semisar)]$^{3+}$ and Δ, Λ, fac-lel$_3$-[Co (NO$_2$)$_2$Me$_3$sar]$^{3+}$, the $-NO_2$ groups were also reduced irreversibly at $E° = -0.68$ V and -0.60 V respectively which are, in both cases, lower than that found in the case of $[Co(dinosar)]^{3+}$ ($E° = -0.46$ V)[4].

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บทคัดย่อ

งานวิจัยนี้ประสพความสำเร็จในการเตรียมสารประกอบเชิงซ้อนซึ่งเกิดจากลิแกนด์ที่มีลักษณะเป็นกรงท่อหุ้ม
ไอออนโคบอลท์(+3)ไว้ในใจกลางกรง ไอออนเชิงซ้อนเหล่านี้ได้แก่ Δ, Λ, fac-lel$_3$-[Co (NO$_2$)$_2$Me$_3$sar]$^{3+}$ (1) (ในที่นี้
(NO$_2$)$_2$Me$_3$sar = 1, 8-dinitro- (4R, 12R, 17R)-trimethyl-3, 6, 10, 13, 16, 19-hexaazabicyclo [6.6.6] eicosane) และ Δ, Λ,
fac-lel$_3$-[Co(Me$_3$sep)]$^{3+}$ (3) (ในที่นี้ (Me$_3$sep) = (4R, 12R, 17R)-trimethyl-1, 3, 6, 8, 10, 13, 16, 19-octaazabicyclo [6.6.6]
eicosane) นอกจากนี้ยังประสพความสำเร็จในการเตรียมสารประกอบเชิงซ้อนซึ่งเกิดจากลิแกนด์ที่มีลักษณะเป็นสามง่ามหรือ
ครึ่งกรงเกาะจับไอออนโคบอลท์(+3)ไว้ ไอออนเชิงซ้อนเหล่านี้ได้แก่ Δ, Λ, fac-lel$_3$[Co(NO$_2$,Me$_3$semisar)]$^{3+}$ (2) (ในที่นี้
(NO$_2$Me$_3$semisar) = tris(((2-aminopropyl) amino)methyl)nitromethane) และ Δ, Λ, fac-lel$_3$-[Co(Me$_3$semisep)]$^{3+}$ (4)
(ในที่นี้ (Me$_3$semisep) = tris(((2-aminopropyl) amino) methyl)amine) สารตั้งต้นที่ใช้ในการเตรียมไอออนเชิงซ้อนประเภท
Δ คือ Δ, fac-lel$_3$-[Co (R)(-)pn $_3$]$^{3+}$ ส่วนสารตั้งต้นที่ใช้ในการเตรียมไอออนเชิงซ้อนประเภท Λ คือ Λ, fac-lel$_3$-[Co (S)(+)pn$_3$]$^{3+}$
ในที่สุดได้ทำการศึกษาสมบัติทางกายภาพของไอออนเชิงซ้อนเหล่านี้ซึ่งเกี่ยวข้องกับ specific rotations, infrared spectra, visible
spectra, nuclear magnetic resonance spectra และ oxidation-reduction potentials