the film on a gold electrode in acetonitrile showing no mass decrease near the first reduction wave as expected. It is worthy to stress that the net mass change is very large compared with previous results. It is due to predominant dissolution of C_{60}^- or C_{60}^{2-} over incorporation of electrolytes as mentioned in a previous paragraph. Accordingly, it supports that the mass decrease near reduction waves in Figure 1(C) is due to the release of solvent molecules.

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Cobalt(III) Complexes of N,N′-Bis(2(S)-aminopropyl)-1(R),2(R)-*trans*-1,2-diaminocyclohexane

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A novel optically active tetraamine ligand possessing four asymmetric centers, N,N′-bis(2(S)-aminopropyl)-1(R),2(R)-*trans*-1,2-diaminocyclohexane (SRRS-apchxn) and its cobalt(III) complexes, $[Co(SRRS\text{-}apchxn)X_2]^{n+}$ ($X=Cl^-$, H_2O, $X_2=CO_3^{2-}$) have been synthesized. This ligand has coordinated stereospecifically to the cobalt(III) ion to give only the Λ-*uns-cis*-(SS) isomer. A trans dichloro complex has been obtained *via* the stereospecific isomerization of Λ-*uns-cis*-(SS)-$[Co(SRRS\text{-}apchxn)Cl_2]^+$ to *trans*-(SS)-$[Co(SRRS\text{-}apchxn)Cl_2]^+$ in CH_3OH-HCl medium. Ligand and complexes have been characterized by electronic absorption, ^1H NMR, CD spectra, and also by elemental analysis. It is of interest that this is one of the few $Co^{III}(N_4)X_2$ type complex preparations, which produces such an *uns-cis* isomer with stereospecificity.

Introduction

The stereochemistry of the metal chelates containing multidentate ligands is an interesting field of study because various chelating modes of those ligands are able to firm a variety of geometrical and optical isomers. The stability of

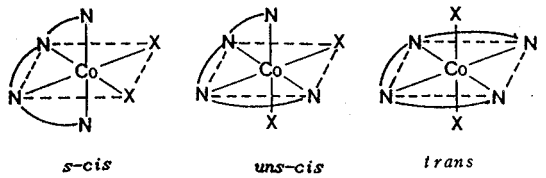
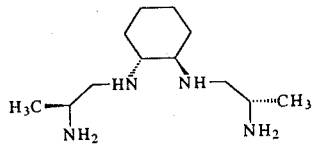


Figure 1. Three possible geometrical isomers of $[Co(trien)X_2]^{n+}$ complexes (Trien: Triethylenetetramine, $NH_2CH_2CH_2NHCH_2$-$CH_2NHCH_2CH_2NH_2$).

these geometrical and optical isomers is dependent on the structure of the ligand. A great deal of publications have described the cobalt(III) complexes of the tetradentate ligands having four nitrogen donor atoms.[1~8]

For some time, we have been studying the stereochemistry of the cobalt(III) complexes of linear flexible tetraamine ligands, and in this work a tetraamine ligand containing four chiral centers, N,N'-bis(2(S)-aminopropyl)-1(R),2(R)-*trans*-1,2-diaminocyclohexane (SRRS-apchxn) has been prepared.



N,N'-bis(2(S)-aminopropyl)-1(R),2(R)-trans-1,2-diaminocyclohexane (SRRS-apchxn)

Three geomertrical isomers, the *s-cis, uns-cis,* and *trans* form, are possible for the metal complexes of the type $[M(N_4)X_2]^{n+}$ (Figure 1). Our reserch focuses on which isomers among the three will be obtained from the cobalt(III) complexes of SRRS-apchxn. It will be shown that the *uns-cis* and *trans* isomers are formed in the preparation of the $[Co(SRRS\text{-}apchxn)X_2]^+$ ($X=Cl^-$, H_2O, $X_2=CO_3^{2-}$), while the *s-cis* isomer is not formed. It is of interest that such a result is one of the few $[Co(N_4)X_2]$ type complex preparations, in which the *s-cis* isomer is not obtained.

Experimental

Trans-1,2-diaminocyclohexane, S-alanine, d-tartaric acid, phthalic anhydride, PCl_5, and $LiAlH_4$ were purchased from Aldrich Chemical Co. and used without further purification.

Electronic absorption spectra were recorded on a Shimadzu UV-240 Double Beam Spectrometer. ^1H NMR spectra were measured with a 270 MHz JEOL GSX-270 Spectrometer and a 80 MHz Varian FT-80A spectrometer. Circular Dichroism spectra obtained from JASCO J-550C Automatic Recording Spectropolarimeter. Elemental analyses were performed by Micro-Tech Analytical Lab., Skokie, Illinois, USA.

Resolution of Trans-1,2-diaminecyclohexane. This was resolved according to the method of Asperger and Liu[9] using d-tartaric acid. $[M]_D^{25}=29.6°$ (0.2 g/mL water).

S-phthaloylalanine. 26.7 g (0.3 mol) of S-alanine and 44.4 g (0.3 mol) of phthalic anhydride was mixed in a beaker and heated in an oil bath at 150 ℃ for 4 hrs. The fused mixture was then cooled to room temperature and recrystallized by using CH_3OH-H_2O (1 : 2 volume ratio) mixed solvent. Yield: 57.0 g (87%)

S-phthaloylalanyl Chloride. 300 mL of benzene was added to an 1 L, three-necked flask equipped with a condenser and was stirred at 50-55 ℃ with magnetic stirrer under nitrogen. 55.5 g (0.25 mol) of S-phthaloylalanine and 52.5 g (0.26 mol) of PCl_5 were gradually added and stirring was continued for 1.5 hrs at 50 ℃. The solution was filtered while hot. The filtrate was concentrated in order to remove the solvent under reduced pressure, and was then vacuum dried to obtain an oil. Yield: 58.3 g (97%)

N,N'-Bis(S-phthaloylalanyl)-1(R),2(R)-*trans*-1,2-diaminocyclohexane. 15.9 g (0.8 mol) $NaHCO_3$, 300 mL of water, and 12.8 g (0.1 mol) of 1(R),2(R)-*trans*-1,2-diaminocyclohexane was mixed in a 1 L three-necked flask and stirred with a magnetic stirrer at −5 ℃. A solution of 53.6 g (0.2 mol) of S-phthaloalanyl chloride in 170 mL of dioxane was slowly added to this solution. Upon the appearance of foam, yellow oil was formed. After 10 min., 200 mL of 2 N HCl was added. The oil phase was collected and dissolved in 95% ethanol. Upon adding hot water, solid products were obtained. Yield: 36.8 g (64%)

N,N'-Bis(S-alanyl)-1(R),2(R)-trans-1,2-diaminocyclohexane dichloride. 31.4 g (0.06 mol) of N,N'-Bis(S-phthaloylalanyl)-1(R),2(R)-*trans*-1,2-diaminocyclohexane was placed in a 1 L flask and a solution of 1 M hydrazine in 150 mL ethanol was added. Additional ethanol was added to make the total volume to be 500 mL. The solution was heated to 80 ℃ and refluxed for 15 hrs. The solvent was removed on distillation. The yellow precipitates were vacuum dried 200 mL of 2 N HCl was added at 50 ℃, then filtered. The filtrate was concentrated to obtain oil, which was washed with chloroform three times, and then vacuum dried. Yield: 17.2 g (87%)

N,N'-Bis(2(S)-aminopropyl)-1(R),2(R)-*trans*-1,2-diaminocyclohexane tetrahydrochloride (SRRS-apchxn·4HCl). 30 mL of THF and 19.0 g (0.5 mol) of $LiAlH_4$ were placed in an 1 L three-necked flask equipped with an mechanical stirrer, a dropping funnel and a reflux condenser under nitrogen in an ice-bath. A solution N,N'-Bis(S-alanyl)-1(R),2(R)-*trans*-1,2-diaminocyclohexane in 100 mL of THF was slowly added. The reaction mixture was heated to 60 ℃ and refluxed for 30 hrs. After cooling to room temperature, 100 mL of water was slowly added. After 30 min., the slurry was filtered and washed with THF. The filtrate and washings were combined. This combined solution was concentrated under reduced pressure and 50 mL of 20% NaOH was added. The free amine was extracted twice by 100 mL of *n*-butyl alcohol, to which 20 mL of conc. HCl was added. The solution was concentrated under reduced pressure and vacuum dried. The crude product was dissolved in 100 mL of methanol. Upon adding ether precipitates were formed, which were collected and washed with ether. Yield: 7.8 g (41%). Anal. Calcd. for $C_{12}H_{28}N_4$·4HCl: C, 38.5; H, 8.6; N, 15.0. Found: C, 38.4; H, 8.7; N, 15.1.

Λ-*uns-cis*-[Co(SRRS-apchxn)(CO_3)]ClO_4. A solution of 4.5 g (1.2×10^{-2} mol) of SRRS-apchxn·4HCl dissolved in 10 mL of water was slowly added to a solution of 4.4 g (1.2×10^{-2} mol) of $Na_3[Co(CO_3)_3]\cdot3H_2O$ in an ice bath. The solution was heated to 55-60 ℃ and then stirred for 20 min. And filtration, 3.0 g (2.4×10^{-2} mol) of $NaClO_4$ was added to pink solution. The solution was concentrated to 10 mL

and 50 mL of ethanol was added. The resultant solution was stored in refrigerator for 2 days, during which period pink precipitates were formed. The pink product was collected by filtration, washed with ethanol and ether, and vacuum dried. Yield: 3.7 g (69%). Anal. Calcd. for $[Co(C_{12}H_{28}N_4)CO_3]ClO_4$: C, 34.6; H, 6.3; N, 12.2. Found: C, 33.9; H, 6.4; N, 12.0.

Λ-*uns-cis*-[Co(SRRS-apchxn)Cl$_2$]ClO$_4$. A suspended solution of 0.54 g (1.2×10^{-3} mol) of Λ-*uns-cis*-[Co(SRRS-apchxn)(CO_3)]ClO_4 in 30 mL of absolute ethanol was placed in an ice bath. HCl gas was bubbled through this solution until all the carbonato complexes were dissolved and became reddish purple in color, which took about 2 min. 0.14 g (1.3×10^{-3} mol) of $LiClO_4$ was added to this solution, which was then filtered. The filtrate was concentrated until crystals were formed. The purple product was filtered and vacuum dried. The reddish purple product was recrystallized from ethanol and ether. Yield: 0.5 g (87%). Anal. Calcd. for $[Co(C_{12}H_{28}N_4)Cl_2]ClO_4$: C, 31.2; H, 6.1; N, 12.1. Found: C, 30.9; H, 6.2; N, 12.0.

Λ-*uns-cis*-[Co(SRRS-apchxn)(H$_2$O)$_2$](ClO$_4$)$_3$. 0.32 g (7.2×10^{-4} mol) of Λ-*uns-cis*-[Co(SRRS-apchxn)(CO_3)]ClO_4 was dissolved in 10 mL of water. 60% $HClO_4$ solution was added until the solution became acidic. The solution was allowed to stand until evolution of CO_2 ceased, which took about 20 min. The pink solution was evaporated until the pink precipitates were formed, which was collected and dried. Yield: 0.4 g (90%). Anal. Calcd. for $[Co(C_{12}H_{28}N_4)(H_2O)_2](ClO_4)_3$: C, 23.0; H, 5.1; N, 8.9. Found: C, 23.2; H, 5.0; N, 9.1.

Isomerization of Λ-*uns-cis*-[Co(SRRS-apchxn)Cl$_2$]$^+$ to *trans*-[Co(SRRS-apchxn)Cl$_2$]$^+$. 0.15 g of Λ-*uns-cis*-[Co(SRRS-apchxn)Cl_2]$^+$ was dissolved in 30 mL of methanol-HCl mixed solution at 20 ℃ and an electronic absorption spectrum was immediately taken. Electronic absorption spectrum of the solution was taken every 5 min. The reddish purple color of the solution began to change to a greenish color and the entire solution changed took green after 1 hr.

Trans-[Co(SRRS-apchxn)Cl$_2$]ClO$_4$. The green solution obtained after the completion of the isomerization described above was allowed to stand for 24 hrs. After an electronic absorption spectrum was taken, the solution was concentrated under reduced pressure until precipitates were formed. The green product was collected upon filtration and recrystallized once from water and ether. Yield: 0.12 g (80%) Anal. Calcd. for $[Co(C_{12}H_{28}N_4)Cl_2]ClO_4$: C, 31.2; H, 6.1; N, 12.1. Found: C, 31.3; H, 5.9; N, 11.9.

Result and Discussion

The ligand, N,N'-Bis(2(S)-aminopropyl)-1(R),2(R)-*trans*-1,2-diaminocyclohexane (SRRS-apchxn) has been synthesized following the synthetic route depicted in Figure 2 using S-alanine and 1(R),2(R)-*trans*-1,2-diaminocyclohexane. The reaction of $Na_3[Co(CO_3)_3]$ with SRRS-apchxn has yield the pink *uns-cis*-[Co(SRRS-apchxn)(CO_3)]$^+$ complex. The substitution reactions of *uns-cis*-[Co(SRRS-apchxn)(CO_3)]$^+$ with HCl and H_2O have yielded, inspectively, reddish purple *uns-cis*-[Co(SRRS-apchxn)Cl_2]$^+$ and pink *uns-cis*-[Co(SRRS-apchxn)(H_2O)$_2$]$^{3+}$. The green *trans*-[Co(SRRS-apchxn)Cl_2]$^+$ complex has

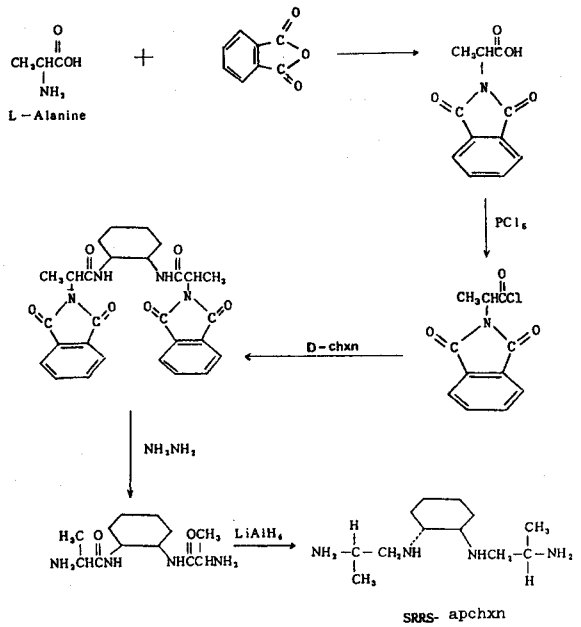


Figure 2. Synthetic route of the optically active ligand, N,N'-bis(2(S)-aminopropyl)-1(R),2(R)-diaminocyclohexane (SRRS-apchxn).

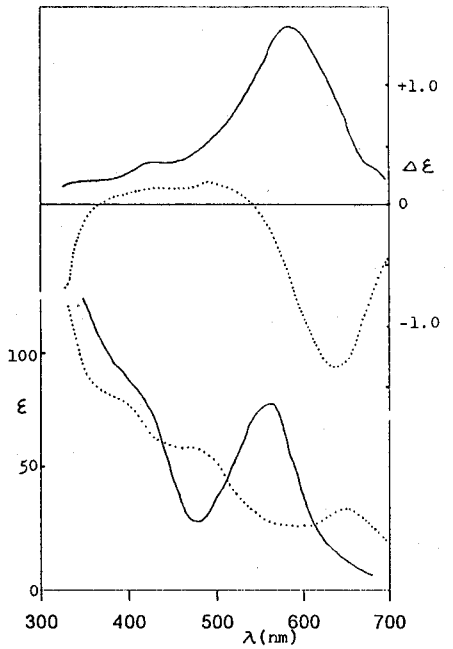


Figure 3. Electronic absorption and CD spectra of *uns-cis*-[Co(L)Cl_2]$^+$ (--) and *trans*-[Co(L)Cl_2]$^+$ (---) (L=SRRS-apchxn).

been prepared as result of the isomerization of the *uns-cis*-[Co(SRRS-apchxn)Cl_2]$^+$ to the *trans* geometry in the CH_3OH-HCl mixed solvent.

The electronic absorption spectrum of the reddish purple dichloro complex (Figure 3) shows that $A_{1g}\rightarrow T_{1g}$ (Oh) transition at 532 nm and the $A_{1g}\rightarrow T_{2g}$ (Oh) transition at 370 nm (Table 1). This dichloro complex does not show a broadened band or a shoulder at near 600 nm, which is typically observed for the *s-cis* isomer.[10,11] The reddish purple dichloro com-

Table 1. λ_{max} for Visible Spectra for Complex Prepared

Compound	I	II	III
Λ-*uns-cis*[Co(SRRS-apchxn)Cl_2]$^+$	532[a]	370	
Λ-*uns-cis*-[Co(SRRS-apchxn)CO_3]$^+$	510	357	
Λ-*uns-cis*-[Co(SRRS-apchxn)$(H_2O)_2$]$^{3+}$	493	355	
Trans-[Co(SRRS-apchxn)Cl_2]$^+$	610	450	380

[a] in nm

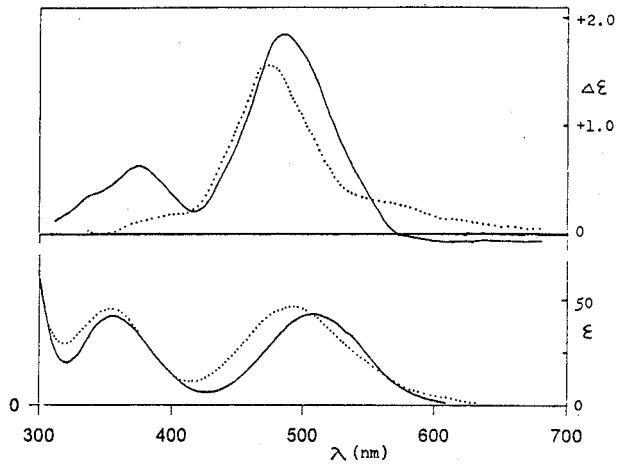


Figure 4. Electronic absorption and CD spectra of Λ-*uns-cis* [Co-(SRRS-baprchxn)CO_3]$^+$ (−), Λ-*uns-cis*-[Co-(SRRS-baprchxn)$(H_2O)_2$]$^{3+}$ (---).

plex prepared in this work has, therefore, the *uns-cis* geometry. The CD curve for this dichloro complex shows that the major $A_1 \rightarrow A_2$ component is positive along with the overlapped $A_1 \rightarrow B_1$ component, which indicate the fact that the *uns-cis* dichloro complex has not only the Λ absolute configuration but also an *uns-cis* geometry.[12~16] The visible absorption and CD spectra of diaqua and carbonato complexes (Figure 4) also suggested that these complexes have the Λ-*uns-cis* configuration. The R absolute configuration of asymmetric centers on the cyclohexane and the CD pattern of the *uns-cis* isomers (Figure 3 and 4) also suggests that the SRRS-apchxn ligand has coordinated stereospecifically to the cobalt (III) ion to give the overall configuration of Λ-*uns-cis*-(SS)-(δ λ λ) isomer.[11~17] The absorption curve of the green dichloro complex (Figure 3) shows the splitting of the $A_{1g} \rightarrow T_{1g}$ (Oh) band as expected for the *trans* geometry.

The dichloro *trans* isomer has been obtained from the isomerization reaction of the *uns-cis*-[Co(SRRS-apchxn)Cl_2]$^+$ complex in the acidic CH_3OH-HCl medium, which is necessary to secure retention of the configuration for the secondary amine groups.

$$\textit{uns-cis}\text{-(SS)-[Co(SRRS-apchxn)}Cl_2]^+ \xrightarrow{CH_3OH\text{-}HCl} \textit{trans}\text{-(SS)-[Co(SRRS-apchxn)}Cl_2]^+$$

Figure 5 shows the spectral changes observed during the isomerization reaction of the *uns-cis* isomer along with three isobestic points at 590, 485, and 412 nm. The CD curve for the *trans* dichloro complex is turned out to be very similar to that of the *trans*-(SS)-[Co(L)Cl_2]$^+$ (L=(S-pm)$_2$,[18] baetchxn[12]),

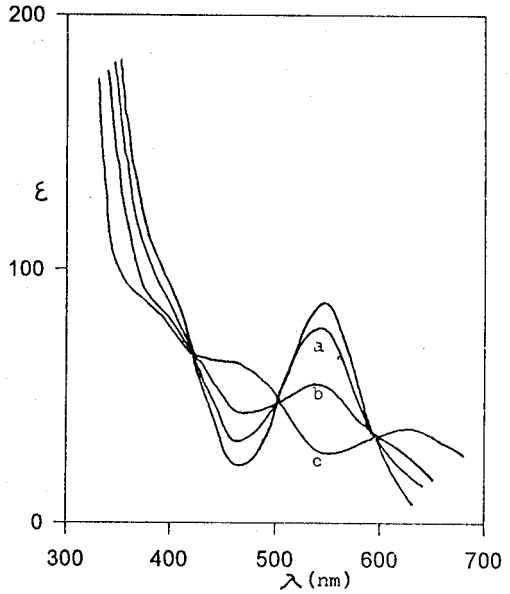


Figure 5. The electronic absorption spectral change for the *uns-cis*-[Co(L)Cl_2]$^+$ to *trans*-[Co(L)Cl_2]$^+$ (L=SRRS-baprchxn): after 5 min (a), 20 min (b), and 1.0 hr.

and shows a dominant negative cotton effect at 597 nm for the $A_{1g} \rightarrow E_g$ (D_{4h}) transition along with a positive cotton effect at 455 nm for the $A_{1g} \rightarrow A_{2g}$ (D_{4h}) transition, which suggests that the *trans* isomer possesses the chelate ring conformation of (δλδ). The stereospecific isomerization reaction observed in this work is due not to the optical inversion in which the absolute configuration at the secondary amines is changed, but to the geometrical inversion only. For such stereospecific isomerization reactions two mechanisms have been suggested; one is an S_N2 mechanism[19] initiated by Cl^- ion in the CH_3OH-HCl solution system and the other an intramolecular rearrangement[12] due to the shift of the terminal NH_2 group. The SRRS-apchxn ligand has shown an interesting spontaneous stereospcificity in is coordination to Co(III) ion as observed in this work. Experimental studies are under way to find out the possibility to obtain optically active *s-cis* geometrical isomers.

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Stability Constants of Divalent Transition and Trivalent Lanthanide Metal Ion Complexes of Macrocyclic Triazatri(Methylacetic Acid)

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The azacrown compound, 1,7-dioxa-4,10,13-triazacyclopentadecane-N,N′,N″-tri(methyl-acetic acid)(N_3O_2-tri(methylacetic acid)) was synthesized by modified procedure of Krespan. Potentiometric method has been used to determine the protonation constants of N_3O_2-tri(methylacetic acid) and stability constants of complexes on the divalent transition metal ions (Co^{2-}, Ni^{2-}, Cu^{2-}, and Zn^{2-}) and trivalent metal ions (Ce^{3+}, Eu^{3+}, Gd^{3+}, and Yb^{3+}) with N_3O_2-tri(methylacetic acid). The stability constants for the complexes of the divalent transition metal ions studied in the present work with N_3O_2-tri(methylacetic acid) were 11.4 for Co^{2+}, 11.63 for Ni^{2+}, 13.51 for Cu^{2+}, and 11.65 for Zn^{2+}, respectively. Thus, the order of the stability constants for complexes on the transition metal ions with N_3O_2-tri(methylacetic acid) was shown $Co^{2-}<Ni^{2-}<Cu^{2-}>Zn^{2-}$ as same as the order of Irving-Williams series. The stability constants of Ce^{3+}, Eu^{3-}, Gd^{3-}, and Yb^{3-} trivalent lanthanide metal ion complexes of N_3O_2-tri(methylacetic acid) were, respectively, 11.26 for Ce^{3-}, 11.56 for Eu^{3-}, 11.49 for Gd^{3+}, and 11.80 for Yb^{3+}. The values of the stability constants on trivalent metal ions with the ligand are increasing according to increase atomic number, due to increase acidity. But the value of stability constant of Gd^{3-} ion is less than the value of Eu^{3+} ion. This disordered behavior is also reported by Moeller.

Introduction

There have been considerable interest in the synthesis of macrocyclic ligands which show high selectivity for a particular metal ion in the complex formation, since such ligands can be used in the fields of biochemistry, hydrometallurgy, and waste treatment.[1~5] The stability constants of the metal ions with macrocyclic ligands were determined by various methods.[6~9]

Delgado *et al.*[10] determined the stability constants of complexes of some divalent and trivalent metal ions with a series of macrocyclic ligands having acetate groups as N-pendant arms. These series of ligands provide an opportunity to study the influence of size of the macrocyclic ring and the increasing number of donor atoms on the stability and selectivity of metal complexes. The metal ions studied include the divalent metal ions, such as Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Ca^{2+}, Pb^{2+}, and trivalent metal ions, such as Al^{3+}, Ga^{3+}, Fe^{3+}, In^{3+}, and Gd^{3+}. These series of ligands also provide an opportunity to compare the affinities of the metal ions studied here with those of the parent N,N′,N″-triazacyclononane-triacetic acid (NOTA), N_3O-triacetic acid, and N_3O_2-triacetic acid, especially

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