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Isomerism of the Metal Complexes Containing Multidentate Ligands. X. $[CoN_6]^{3+}$-Type Complexes Containing $H_2N(CH_2CH_2NH)_nH$ (n=0—4)

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The preparation, separation, and characterization of isomeric complexes of type $[CoN_6]^{3+}$, containing one, two, or three molecules of NH_3, en, dien, trien, and tetren (n=0, 1, 2, 3, and 4, respectively for $H_2N(CH_2CH_2NH)_nH$) are reported. All the possible five stereoisomers for $[Co(NH_3)(en)(dien)]^{3+}$ and six stereoisomers for $[Co(en)(trien)]^{3+}$ have been successfully isolated, but only three of four possible geometrical isomers could be obtained for $[Co(NH_3)(tetren)]^{3+}$. These were characterized by electronic, circular dichroism (CD), and $^{13}C\{^1H\}$ NMR spectroscopy. Conformational analyses were, also, carried out and the stability, or formation of each isomer at the equilibrium state, is discussed from the calculated strain-energy data and experimental formation ratios.

Linear polyamines, $H_2N(CH_2CH_2NH)_nH$ (n=1—5)[1)] coordinate to metal ions and the resulting coordination compounds contain only the five-membered chelate rings which are the most frequently found in metal complexes. Table 1 lists all the complexes of $[CoN_6]^{3+}$-type containing the polyamine ligand(s) and NH_3 (n=0).

Presently we are reporting the isomerism of the complexes, V, VI, IX, and X (Table 1). In the course of this study, the structures of both the geometrical isomers of $[Co(NH_3)_3(dien)]^{3+}$ have been determined by three-dimensional X-ray analysis.[6)] The $^{13}C\{^1H\}$ NMR spectrum of the mer isomer was also reported.[12)] The isomers of the complex, $[Co(NH_3)(en)(dien)]^{3+}$ are newly prepared in the present study. $[Co(NH_3)_2(trien)]^{3+}$ and $[Co(NH_3)(tetren)]^{3+}$ were prepared by Basolo[8)] and Schlessinger,[13)] respectively. $[Co(en)(trien)]^{3+}$ was studied by Schaefer and Brubaker.[10)] However, all of their isomers were not isolated in these studies. Recently, we succeeded in isolating not only the six cis isomers, but also all of the three possible trans isomers of $[Co(NH_3)_2(trien)]^{3+}$.[9)]

Isolation of each isomer was mainly performed by column chromatography on Sephadex ion exchanger.[14)] The empirical elution rules that we reported,[15)] were often effectively used for the assignment of geometrical isomers.

Experimental

Materials. The amines, $H_2N(CH_2CH_2NH)_nH$ (n=1—4) were obtained from Wako Pure Chemical Industries, LTD. and all other chemicals commercially available were used without further purification unless otherwise stated.

(i) $[Co(NH_3)_3(dien)]X_3$: To 25 cm³ of a 3 M (=mol dm^{-3}) aqueous ammonia solution, 1.3 g of *mer*-$[CoCl_3(dien)]$,[16)] 5 g of NH_4Cl, and 0.2 g of activated charcoal were added, and the mixture was stirred for 2 h. The activated charcoal

Table 1. Isomers of $[CoN_6]^{3+}$-Type Complexes Containing $H_2N(CH_2CH_2NH)_nH$ (n=0—5)

	Complexes	Number of Geometrical Isomers[a)]	Number of Optical Isomers	Total Number of Isomers	Ref.
I.	$[Co(NH_3)_6]^{3+}$	1	0	1	2
II.	$[Co(NH_3)_4(en)]^{3+}$	1	0	1	3
III.	$[Co(NH_3)_2(en)_2]^{3+}$	2	1	3	4
IV.	$[Co(en)_3]^{3+}$	1	1	2	5
V.	$[Co(NH_3)_3(dien)]^{3+}$	2	0	2	6
VI.	$[Co(NH_3)(en)(dien)]^{3+}$	4	1	5	This work
VII.	$[Co(dien)_2]^{3+}$	3	2	5	7
VIII.	$[Co(NH_3)_2(trien)]^{3+}$	5	4	9	8, 9
IX.	$[Co(en)(trien)]^{3+}$	3	3	6	8, 10
X.	$[Co(NH_3)(tetren)]^{3+}$	8	7	15	This work
XI.	$[Co(linpen)]^{3+}$	8	8	16	11

a) All the possible existent conformational isomers, based on the configuration about a secondary amine nitrogen are included.

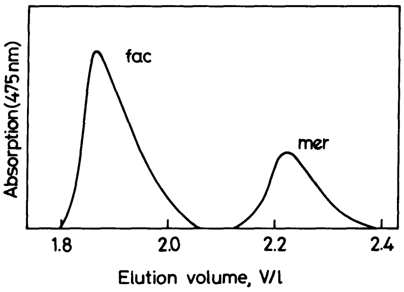

Fig. 1. Elution curve of $[Co(NH_3)_3(dien)]^{3+}$. ϕ2.7× 140 cm SP-Sephadex (C-25); 0.18 M Na_2SO_4.

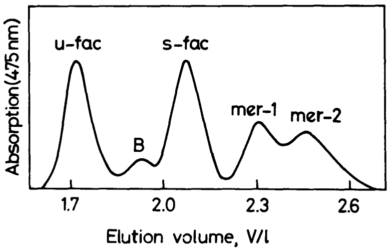

Fig. 2. Elution curve of $[Co(NH_3)(en)(dien)]^{3+}$. ϕ2.7 × 140 cm SP-Sephadex (C-25); 0.18 M Na_2SO_4.

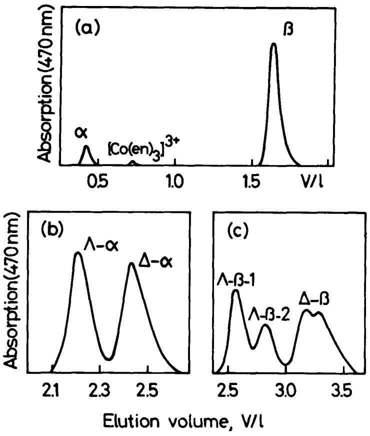

Fig. 3. Elution curves of $[Co(en)(trien)]^{3+}$. ϕ2.7× 130 cm SP-Sephadex (C-25); (a) 0.1 M Na_3PO_4, (b) 0.18 M sodium (+)tartrate, (c) 0.13 M sodium (+) tartratoantimonate(III).

was filtered off and the filtrate was acidified with hydrochloric acid. The resulting solution was diluted with a large amount of water and passed over a pre-column of SP-Sephadex (C-25).[14] A portion of the SP-Sephadex charged with the product was poured on the top of an SP-Sephadex column (ϕ2.7×140 cm) and the adsorbed complexes were eluted with 0.18 M Na_2SO_4. The elution curve is shown in Fig. 1. The effluents of two elution bands were separately collected and diluted with 0.01 M HCl about twenty times, and then each diluted solution was passed through a short column of SP-Sephadex previously conditioned with 1 M HCl and the complex was adsorbed on it. After the adsorbed column being washed with a large amount of 0.01 M HCl to remove sodium ions, the complex isomer was eluted with 1 M HCl. The chlorides of the complex were obtained by evaporating the eluate to dryness under reduced pressure, over P_2O_5 and NaOH.

(ii) $[Co(NH_3)(en)(dien)]X_3$: (*a*) To 25 cm³ of a 0.5 M aqueous ammonia solution, 1.5 g of *s-fac*-$[CoCl(en)(dien)]Cl_2$,[17] 5 g of NH_4Cl, and 0.2 g of activated charcoal were added, and the suspension was stirred for 12 h.

(*b*) Using *mer*-$[CoCl_3(dien)]$ as a starting material: The mixture of 0.52 g of *mer*-$[CoCl_3(dien)]$, 0.26 g of en·2HCl, and 10 cm³ of a 0.5 M aqueous ammonia solution was stirred for 48 h with 0.05 g of activated charcoal. The reaction products were processed in a similar manner a in (*i*). The resulting elution curves are shown in Fig. 2. The u-fac isomer was separated into two bands by elution with a 0.15 M sodium (+)tartratoantimonate(III) solution. The chlorides of each isomer were obtained as in (*i*). The B band is that of *fac*-$[Co(NH_3)_3(dien)]^{3+}$.

(iii) $[Co(en)(trien)]X_3$: $[Co(en)(trien)]Cl_3$ was prepared from $[CoCl_2(trien)]Cl$ and ethylenediamine, following the method of Schaefer and Brubaker.[10] The resulting solution of the chloride mixture was subjected to SP-Sephadex chromatography (Fig. 3a). The α isomer easily isomerizes to the β isomers in an alkaline solution. Each isomer was resolved as shown in Fig. 3b and c. The two optically active β isomers could be more effectively isolated from each pure *racemic* β isomer, which was previously separated from each other by recycling chromatography using a mixture of 0.15 M Na_2SO_4 and 0.01 M HCl as eluent.

(iv) $[Co(NH_3)(tetren)]X_3$: (*a*) $[Co(NH_3)(tetren)]Cl_3$ was prepared from $[CoCl(NH_3)_5]Cl_2$ and tetren·5HCl, as described below. The ligand hydrochloride was purified twice by recrystallization from water. To 20 cm³ of concentrated aqueous ammonia solution containing 2.5 g of $[CoCl(NH_3)_5]Cl_2$,[18] 4.3 g of tetren·5HCl and 0.5 g of activated charcoal were added, and the mixture was stirred for 15 h. The filtrate was diluted with 0.01 M HCl and passed through an SP-Sephadex column. The elution curve is shown in Fig. 4a, where the A, C-1, and C-2 bands were assigned to those of the isomers of $[Co(NH_3)(tetren)]^{3+}$ from their $^{13}C\{^1H\}$ NMR spectra and the others to those of impurities. These C-1 and C-2 bands were not separated by the elution with a neutral or basic eluent. The C-2 isomer formed also by the isomerization of the C-1 in an aqueous solution, but it was difficult to obtain purely because of its low formation ratio and low stability. The optical resolution of the C-1 isomer was attained by elution with 0.15 M sodium (+)tartratoantimonate(III) in a similar manner as in Fig. 3b.

(*b*) $[CoCl(tetren)](ClO_4)_2$[19] was allowed to react with liquid ammonia. Since only one geometrical isomer (C in the preceding (*a*)) could be obtained from "α-$[CoCl(tetren)](ClO_4)_2$,"[19] the following compound was used as starting material in order to get other isomers. The filtrate, in Method B of House and Garner,[19] after removing the first precipitated tetrachlorozincate(II) salt was allowed to stand for a month. The additionally formed tetrachlorozincate(II) crystals were changed to the perchlorate salt. To about 20 cm³ of liquid ammonia, 1 g of the perchlorate was added. The excess ammonia was allowed to evaporate (slowly) at room temperature. An aqueous solution of the

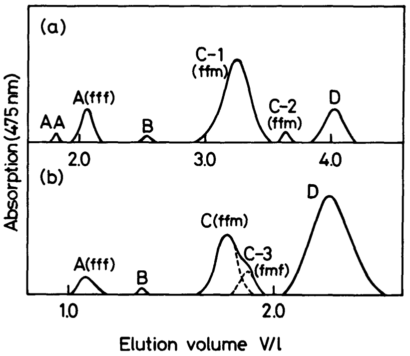

Fig. 4. Elution curves of $[Co(NH_3)(tetren)]^{3+}$ from different origin. ϕ2.7 × 140 cm SP-Sephadex (C-25); (a) 0.15 M Na_2SO_4–0.01 M HCl, (b) 0.18 M Na_2SO_4.

orange residue was passed through an SP-Sephadex column (Fig. 4b). In Fig. 4b, the B and D bands are those of impurities. The C-3 isomer was completely separated into two portions by the elution with a 0.15 M sodium (+)tartratoantimonate(III) solution.

(*c*) The reaction of $[Co(NO_3)(NH_3)_5](NO_3)_2$ with tetren in DMSO (70—80 °C), and the reaction of $[CoCl(tetren)]ZnCl_4$ with ammonia in the presence of NH_4Cl and activated charcoal in an aqueous solution, were also used. Their chromatograms were similar to that in Fig. 4a.

Physical Measurements. Absorption spectra were obtained with a Union Giken SM 401 spectrophotometer equipped with a 1 cm quartz cell at 25 °C. The sample solutions contained the complex ions in 10^{-3}—10^{-2} M concentrations. CD spectra were measured for an approximately 10^{-3} M solution of each isomer in 0.01 M HCl, with a JASCO model J-20 or J-40 spectropolarimeter using a 1 cm cell. $^{13}C\{^1H\}$ NMR spectra were recorded on a JEOL JNM-FX60 spectrometer at a probe temperature of 35 °C. The solvent used was a 0.01 M HCl solution. Dioxane in D_2O in a coaxial inner tube was used as an external reference for all samples.[20)]

Identification of Compositions. $^{13}C\{^1H\}$ NMR spectra were measured for the prepared metal complexes. The expected number of carbon atoms and/or the symmetry of the isomer was confirmed from their relative intensities of carbon signals. Elemental analyses were also performed for the hexacyanocobaltates of newly isolated isomers, which could be easily isolated from the solution due to their low solubilities. The agreement between the calculated and found values was within the usual limit of variation of elemental analysis.

Results and Discussion

Figures 5—8 show the possible geometrical and conformational isomers of the complexes, V, VI, IX, and X. The two isomers of $[Co(NH_3)_3(dien)]^{3+}$, the s-fac and two mer isomers of $[Co(NH_3)(en)(dien)]^{3+}$, and the fff isomer of $[Co(NH_3)(tetren)]^{3+}$ have plane-symmetric, that is, nonresolvable structures, but the others can be resolved into their optical isomers. As can be seen from Figs. 1—4, we could isolate all the possible number of stereoisomers, i.e., 2, 5, and 6 for $[Co(NH_3)_3(dien)]^{3+}$, $[Co(NH_3)(en)(dien)]^{3+}$, and $[Co(en)(trien)]^{3+}$, respectively, but only three of four possible geometrical isomers of $[Co(NH_3)(tetren)]^{3+}$. All the four fmm conformational isomers, which were different in the configuration of two secondary nitrogen atoms in the center of the meridional structures, could not be isolated in the present study. The structure of each isomer was assigned mainly on the basis of the elution order[15)] and $^{13}C\{^1H\}$ NMR spectrum.

The empirical elution rules predict that the complex isomer with higher ability to associate with eluent anions is eluted faster than the other(s).

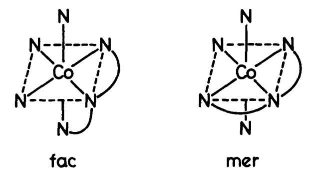

Fig. 5. Possible geometrical isomers of $[Co(NH_3)_3(dien)]^{3+}$.

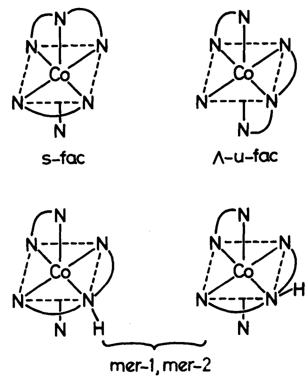

Fig. 6. Possible geometrical and conformational isomers of $[Co(NH_3)(en)(dien)]^{3+}$.

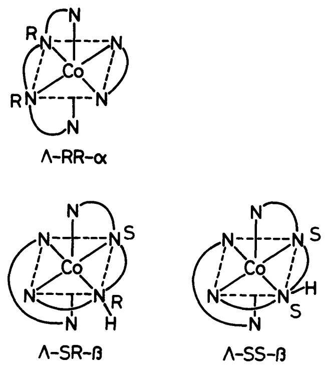

Fig. 7. Possible geometrical and conformational isomers of $[Co(en)(trien)]^{3+}$.

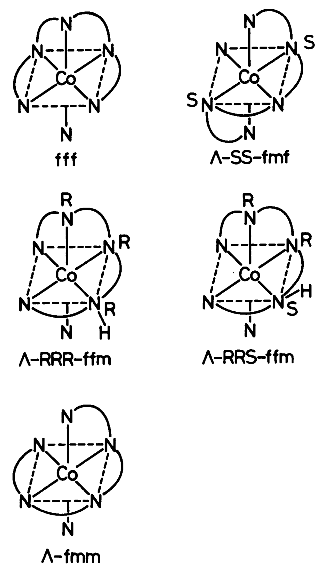

Fig. 8. Geometrical and conformational isomers of $[\mathrm{Co(NH_3)(tetren)}]^{3+}$.
The absolute configuration, *R* or *S* of the central nitrogen atom of tetren in the ffm isomers, was determined assuming that the priority[24)] of the the *facial* structure as substituent is higher than that of the *meridional* structure. All the four possible existent conformational isomers were abbreviated for the fmm structure.

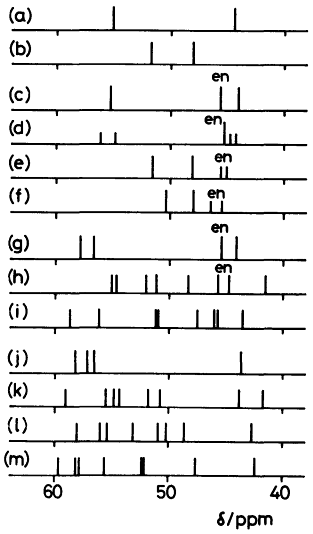

Fig. 9. Diagramatic representation of the $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR spectra of $[\mathrm{CoN_6}]^{3+}$-type complex isomers. (a) *fac*-; (b) *mer*-$[\mathrm{Co(NH_3)_3(dien)}]\mathrm{Cl_3}$; (c) *s-fac*-; (d) *u-fac*-; (e) *mer-1*-; (f) *mer-2*-$[\mathrm{Co(NH_3)(en)(dien)}]\mathrm{Cl_3}$; (g) α-; (h) *β*-1-; (i) *β-2*-$[\mathrm{Co(en)(trien)}]\mathrm{Cl_3}$; (j) *fff*-; (k) *fmf*-; (l) *ffm*(C-1)-; (m) *ffm*(C-2)-$[\mathrm{Co(NH_3)(tetren)}]\mathrm{Cl_3}$. The signals with "en" are those of ethylenediamine.

Therefore, it can be easily explained that the fac of $[\mathrm{Co(NH_3)_3(dien)}]^{3+}$ (Fig. 1), the u-fac and then the s-fac of $[\mathrm{Co(NH_3)(en)(dien)}]^{3+}$ (Fig. 2), the α of $[\mathrm{Co(en)(trien)}]^{3+}$ (Fig. 3), and the fff isomer of $[\mathrm{Co(NH_3)(tetren)}]^{3+}$ (Fig. 4), elute faster than the other isomers with meridional structures.

Figure 9 shows the diagramatic representation of $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR spectra of all the present isomers. Since the aforementioned isomers including *mer*-$[\mathrm{Co(NH_3)(en)(dien)}]^{3+}$ (C_s symmetry), and α-$[\mathrm{Co(en)(trien)}]^{3+}$ (C_2 symmetry), have two equivalent carbons, the number of the NMR signals is reduced to one-half of that of the other asymmetric isomers. The two carbon atoms of ethylenediamine in *mer*-$[\mathrm{Co(NH_3)(en)(dien)}]^{3+}$ are not equivalent and therefore show two different signals at the corresponding magnetic field. In general, the NMR signal of the carbon adjacent to a primary nitrogen atom appears at higher magnetic field than those adjacent to a secondary nitrogen atom.[21)] This tendency is more pronounced in the fac configuration than in the mer, because of the less-strained valence angles about the secondary nitrogen atom of the former. Thus such isomeric structures are easily distinguished with each other in terms of the NMR signals.

The structures of the two *β*-$[\mathrm{Co(en)(trien)}]^{3+}$ isomers, *β-1* and *β-2*, were assigned to (*Λ-SS,Δ-RR*) and (*Λ-SR,Δ-RS*), respectively, by comparison of their NMR signals with those of *cis*-*β*-$[\mathrm{Co(NH_3)_2(trien)}]^{3+}$.[8)] The spectra of the C-1 isomer in Fig. 4a was very similar to that of (*Λ-RRS,Δ-SSR*)-*ffm*-$[\mathrm{CoCl(tetren)}](\mathrm{ClO_4})_2$, the structure of which was determined by X-ray analysis.[22)] Therefore, the C-1 was assigned to the above structure and the C-2 to (*Λ-RRR,Δ-SSS*)-ffm structure. The optical resolution of these isomers is consistent with assignment to the resolvable structures.

The data of absorption spectra in the visible region are summarized in Table 2 together with those of CD spectra (Fig. 10) of the optically active isomers. The positions of the first and second absorption maxima of the complexes are normal as those for the $[\mathrm{CoN_6}]^{3+}$-type ones. The molar extinction coefficients, ε of the isomers with *meridional* structure are larger than those of the *facial* ones. It may be attributed to the distorsion from a regular octahedron in mer isomers. The absolute configurations of the optically active isomers were assigned according to the sign of the dominant CD component at the first absorption band region, that is, the plus sign to the *Λ* configuration.

Table 3 shows the results of the conformational analysis for all the possible isomers of the relevant complexes. The strain-energy minimization calculation was carried out by using a modification of the computer program of Boyd.[9b,23)] A tendency, that fac isomers or structures are less-strained in angle bending and more-strained in torsional interaction than mer ones, can be seen for the isomers except [Co(NH$_3$)(tetren)]$^{3+}$. Among the isolated isomers of each complex, there is a good correlation between the formation ratio and the strain energy, considering the statistical effects on some configurational structures. The strain-energy differences are rather small among the isomers of the complexes, the entire set of isomers of which could be isolated from the reaction mixtures.

Unambiguous assignment of the *mer*-[Co(NH$_3$)(en)(dien)]$^{3+}$ was difficult to make either from the conformational analysis, or from the elution order, or from the ^{13}C{^{1}H} NMR spectroscopy.

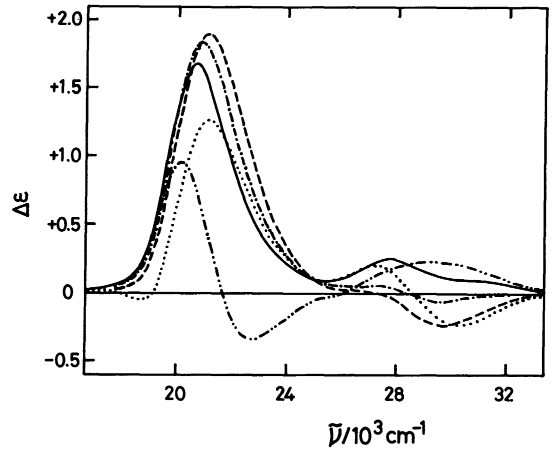

Fig. 10. Circular dichroism spectra of *Λ-u-fac*-[Co(NH$_3$)(en)(dien)]$^{3+}$(—··—), *Λ(SS)-β-1*-[Co(en)(trien)]$^{3+}$(—·—), *Λ(SR)-β-2*-[Co(en)(trien)]$^{3+}$(----), *Λ(SS)-fmf*-[Co(NH$_3$)(tetren)]$^{3+}$(——), and *Λ(RRS)-ffm*-[Co(NH$_3$)(tetren)]$^{3+}$(····).

Table 2. Absorption and CD Spectral Data

Complexes	Absorption		CD	
	$\tilde{\nu}$/cm^{-1}	ε	$\tilde{\nu}$/cm^{-1}	$\Delta\varepsilon$
fac-[Co(NH$_3$)$_3$(dien)]$^{3+}$	21140	82		
	29500	70		
mer-[Co(NH$_3$)$_3$(dien)]$^{3+}$	21190	105		
	29240	79		
s-fac-[Co(NH$_3$)(en)(dien)]$^{3+}$	21190	95		
	29540	85		
u-fac-[Co(NH$_3$)(en)(dien)]$^{3+}$	21410	75	20120	+0.96
(*Λ*)	29590	65	22680	−0.35
			29330	+0.22
mer-1-[Co(NH$_3$)(en)(dien)]$^{3+}$	21370	113		
	29370	86		
mer-2-[Co(NH$_3$)(en)(dien)]$^{3+}$	21280	111		
	29150	80		
α-[Co(en)(trien)]$^{3+}$	21370	88	20370	+2.42
(*Λ-RR*)	29590	82	22990	−0.53
			28330	+0.56
β-1-[Co(en)(trien)]$^{3+}$	21320	123	20880	+1.84
(*Λ-SS*)	29410	99	27170	+0.05
			29590	−0.06
β-2-[Co(en)(trien)]$^{3+}$	21140	135	21140	+1.81
(*Λ-SR*)	29330	113	29590	−0.23
fff-[Co(NH$_3$)(tetren)]$^{3+}$	21190	80		
	29410	61		
ffm-[Co(NH$_3$)(tetren)]$^{3+}$	21100	126	17120	+0.02
(*Λ-RRS*, C-1)	29100	88	18730	−0.05
			21140	+1.27
			27250	+0.20
			30210	−0.23
fmf-[Co(NH$_3$)(tetren)]$^{3+}$	21190	129	20700	+1.68
(*Λ-SS*)	29240	108	27700	+0.26

Table 3. Minimized Energy Terms (kJ mol^{-1}) for the Isomers of [CoN$_6$]$^{3+}$-Type Complexes

Complexes	Bond Stretching	Nonbonded Interaction	Angle Bending	Torsion	Total
fac-[Co(NH$_3$)$_3$(dien)]$^{3+}$	2.8	2.6	6.6	15.3	27.3
mer-[Co(NH$_3$)$_3$(dien)]$^{3+}$	3.2	4.7	12.5	10.6	31.0
s-fac-[Co(NH$_3$)(en)(dien)]$^{3+}$	3.5	4.2	8.7	16.9	33.3
u-fac-[Co(NH$_3$)(en)(dien)]$^{3+}$	2.9	3.1	7.8	19.7	33.5
mer-1-[Co(NH$_3$)(en)(dien)]$^{3+}$	3.4	3.7	13.0	13.8	33.9
mer-2-[Co(NH$_3$)(en)(dien)]$^{3+}$	3.2	3.0	12.7	14.2	33.1
α-[Co(en)(trien)]$^{3+}$	4.0	10.5	11.9	29.4	55.8
β-1-[Co(en)(trien)]$^{3+}$(*Λ-SS*)	4.0	6.5	14.5	22.9	47.9
β-2-[Co(en)(trien)]$^{3+}$(*Λ-SR*)	4.0	5.9	17.8	21.7	49.4
fff-[Co(NH$_3$)(tetren)]$^{3+}$	3.5	8.3	10.8	33.6	56.2
ffm-[Co(NH$_3$)(tetren)]$^{3+}$(*Λ-RRS*)	3.9	8.1	16.1	26.9	55.0
ffm-[Co(NH$_3$)(tetren)]$^{3+}$(*Λ-RRR*)	4.8	10.4	20.5	25.7	61.4
fmf-[Co(NH$_3$)(tetren)]$^{3+}$	4.3	12.7	15.6	31.1	63.7
fmm-1-[Co(NH$_3$)(tetren)]$^{3+}$(*Λ-SSS*)	4.5	14.1	17.6	33.8	70.0
fmm-2-[Co(NH$_3$)(tetren)]$^{3+}$(*Λ-SSR*)	4.4	12.0	27.0	23.6	67.0
fmm-3-[Co(NH$_3$)(tetren)]$^{3+}$(*Λ-SRS*)	4.3	10.4	28.3	24.3	67.3
fmm-4-[Co(NH$_3$)(tetren)]$^{3+}$(*Λ-SRR*)	4.3	11.0	20.6	33.9	69.8

The $[Co(NH_3)(tetren)]^{3+}$ complexes, the hitherto undetected fmm isomers will be much more strained than all the others from strain energy calculation. Even if the fmm isomers existed in the solution, it would be hard to detect or isolate them, because of their small content and low stability.

Thus, among the isomers of $[CoN_6]^{3+}$-type listed in Table 1, only those of fmm type of $[Co(NH_3)(tetren)]^{3+}$ remained to be detected and isolated.

References

1) The following abbreviations will be used in the present paper: en=ethylenediamine (n=1); dien=diethylenetriamine (n=2); trien=triethylenetetramine (n=3); tetren=tetraethylenepentamine (n=4); linpen=linear pentaethylenehexamine (n=5).

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