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CONFORMATIONAL ANALYSIS AND ISOLATION OF THE ISOMERS OF $[Co(hexaen)]^{3+}$

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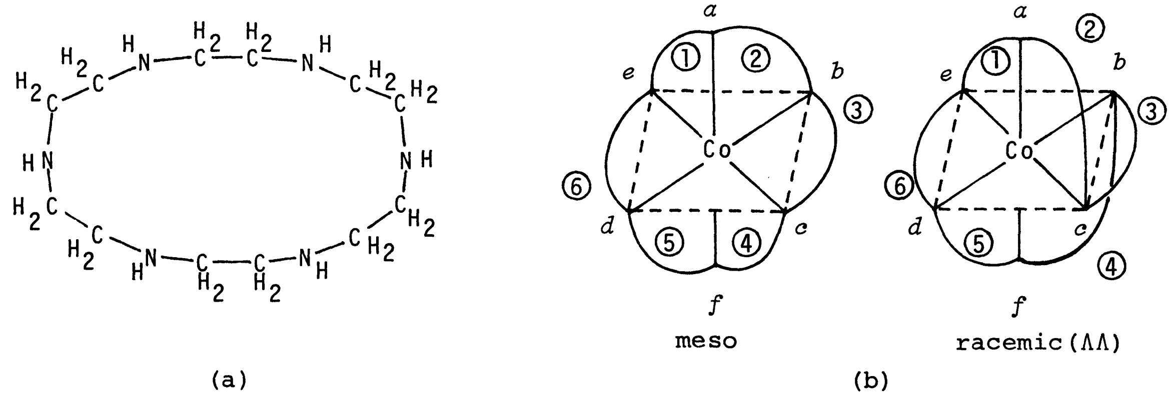
The conformational analysis of the meso and two racemic isomers of $[Co(hexaen)]^{3+}$(Fig. 1) has been carried out and their energy-minimized structures have been determined. Based on these results, the isolation of the three isomers was achieved.

In the previous paper[1)] the conformational analysis of the $[Co(linpen)]^{3+}$ (linpen = $H_2N(CH_2CH_2NH)_4CH_2CH_2NH_2$) isomers was carried out and the comparison of the experimental and calculated formation ratios of those isomers suggested that this technique was applicable to the assignment of the structures of the configurational and conformational isomers. Furthermore this technique was also used to characterize the isomers of $[Co(en)(Meen)_2]^{3+}$(Meen = N-methylethylenediamine),[2)] and $[Co(dien)(dema)]^{3+}$ and $[Co(dema)_2]^{3+}$(dema = N-methylbis-(2-aminoethyl)amine)[3)] ions.

We now report on the results of the conformational analysis of the cobalt(III) complex containing cyclic hexaethylenehexamine(abbreviated as hexaen, Fig. 1a). As Fig. 1b shows, in the $[Co(hexaen)]^{3+}$ ion, meso and racemic forms are possible.



(a) (b)

Fig. 1 Hexaen(a) and the geometric isomers of $[Co(hexaen)]^{3+}$(b).

The meso(ΔΛ) isomer is composed of both Δ- and Λ-$[Co(en)_3]^{3+}$-type structures which correspond to two respective configurations containing three alternate chelate rings of the six. The racemate is resolvable to ΔΔ and ΛΛ isomers which are composed of two Δ- and two Λ-$[Co(en)_3]^{3+}$-type structures respectively. These meso and racemic isomers with only one configurational asymmetric center (cobalt(III) ion in this case) will give new-type isomerism. No examples have ever been reported on the isolation of both isomers.

From consideration of a molecular model, the meso isomer[4)] has the high-symmetrical(D_{3d}) and rigid structure with little strain. However this structure has so large non-bonded hydrogen-hydrogen interactions that it is not realistic. When the conformational analysis of the meso isomer is initiated from this D_{3d} structure, using the same parameters as for the isomers of $[Co(linpen)]^{3+}$,[1)] it converges on that with C_3 symmetry. In this energy-minimized structure(Table 1), the Co-N bond distances are longer than the initial one(1.970 Å) and the two N-C bond distances in each chelate ring are distinct from one another(1.503 and 1.489 Å), which can avoid some large hydrogen-hydrogen non-bonded interactions as in the initial structure. The energy terms are presented in Table 2.

Table 1. Molecular geometries of the isomers of $[Co(hexaen)]^{3+}$(Fig. 1b)

Isomer	Bond length Co-N						Valency angle ∠NCoN (Dihedral angle ∠NCCN) chelate ring					
	N(*a*)	N(*b*)	N(*c*)	N(*d*)	N(*e*)	N(*f*)	1	2	3	4	5	6
meso	1.993	1.993	1.992	1.992	1.993	1.992 Å	85.0 (+42.8)	85.0 (-42.7)	84.9 (+42.7)	85.2 (-42.9)	85.0 (+42.8)	85.0° (-42.8°)
rac-1	1.957	1.981	1.973	1.973	1.982	1.957	83.7 (-37.7)	85.3 (+45.1)	88.6 (-45.7)	83.8 (-37.5)	85.4 (+45.1)	88.6 (-45.7)
rac-2	1.957	1.973	1.973	1.988	1.988	1.956	85.5 (+47.9)	83.4 (-35.9)	89.4 (-49.7)	83.4 (-35.9)	85.5 (+47.9)	87.0 (-39.8)

Table 2. Energy terms for the isomers of $[Co(hexaen)]^{3+}$

Isomer	Bond	Nonbond	Angle	Torsion	Total
meso	14.4	61.4	32.9	46.4	155.1 kJ/mol
rac-1	7.7	45.1	42.0	45.3	140.1
rac-2	8.3	47.0	39.7	45.6	140.6

On the other hand, the racemic isomers contain two >NH groups of the meridional structure, and the more stable isomers have the structures whose conformations of chelate rings are λδλλδλ(rac-1) and δλλλδλ(rac-2) in the order of chelate rings in Fig. 1b, for the ΛΛ configurations. The conformational analysis of the racemic isomers was carried out, using these two structures possessing C_2 symmetry as the initial ones. The results are presented in Tables 1 and 2. The energy-minimized structures of two racemic isomers retain the C_2 symmetry, and the total energies are similar to each other and 15 kJ/mol lower than that of the meso isomer.

The $[Co(linpen)]^{3+}$ ion is composed by adding an ethylenegroup($-CH_2CH_2-$) instead of two hydrogen atoms to the $[Co(dien)_2]^{3+}$ ion. The increase of the total minimized energies is on the average 34 kJ/mol, and 44 kJ/mol for the most unstable isomer whose total energy is 20 kJ/mol higher than the most stable one. The $[Co(hexaen)]^{3+}$ ion has one more $-CH_2CH_2-$ groups than the $[Co(linpen)]^{3+}$ ion. In this case the increases of energy will be larger than 34 kJ/mol because the crowdedness in $[Co(hexaen)]^{3+}$ compared to $[Co(linpen)]^{3+}$ is heavier than that in $[Co(linpen)]^{3+}$ compared to $[Co(dien)_2]^{3+}$. The total minimized energies of the racemic and meso isomers of $[Co(hexaen)]^{3+}$ are 35 and 50 kJ/mol more than the average one of $[Co(linpen)]^{3+}$ isomers, and the difference between the energies of the both isomers is not very large. Therefore it is concluded that two of the racemic isomers and meso isomer are stable enough to form and be isolated.

Based on the results of the preceding conformational analysis, we tried to isolate the isomers of $[Co(hexaen)]^{3+}$. The complex was prepared by the reaction of hexaen with $[Co(H_2O)(NH_3)_5]_2(SO_4)_3$ in an aqueous solution. The resulting solution was subjected to column chromatography on SP-Sephadex. The elution curve by means of a 0.18 M Na_2SO_4-0.01 M HCl solution is shown in Fig. 2a.

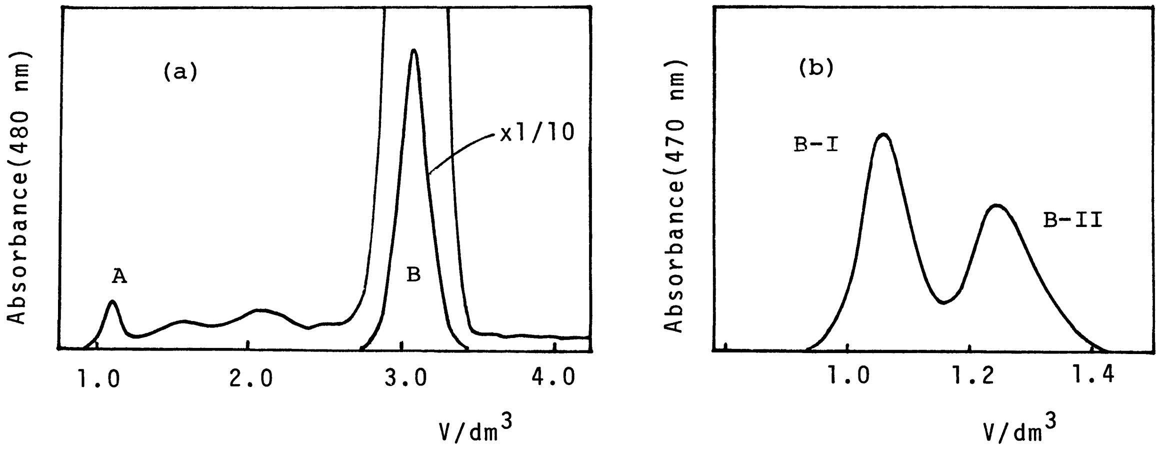


Fig. 2 Elution curves of the isomers of $[Co(hexaen)]^{3+}$(∿25 °C): (a) ϕ2.7X146 cm column, 0.18 M Na_2SO_4-0.01 M HCl; (b) ϕ2.7X40 cm column, 0.1 M Na_2SO_4-0.2 M H_2SO_4.

The elemental analysis data showed that the chlorides of complexes in the A and B bands had the chemical composition of $[Co(hexaen)]Cl_3 \cdot nH_2O$ (n = 0 in A, n = 2.5 in B). The A band is much smaller(<1 %) than the B band. The complex in the latter could be partially resolved by chromatography with a 0.18 M sodium (+)-tartrate or 0.15 M sodium (+)-tartratoantimonate(III) solution as the eluent. Figure 3 shows ^{13}C NMR spectra of these isomers in a 0.01 M HCl aqueous solution. From the above results it is concluded that the A and B bands are meso and racemic isomers respectively. The meso isomer shows only one ^{13}C NMR signal(Fig. 3a). It seems that this isomer does not retain the C_3 structure obtained by the conformational analysis and has the D_{3d} symmetry on the average because each chelate ring rapidly changes its structure in an aqueous solution. The ^{13}C NMR spectrum(Fig. 3b) and the results for the conformational analysis of the racemic isomers suggests that the B band consists of a mixture of two conformational isomers with the C_2 symmetry. Actually this band could be separated into two by elution with a 0.1 M Na_2SO_4-0.2 M H_2SO_4 solution (Fig. 2b). Further details on the experimental results containing the determination of the structures by the X-ray crystal analysis will be reported in the near future.

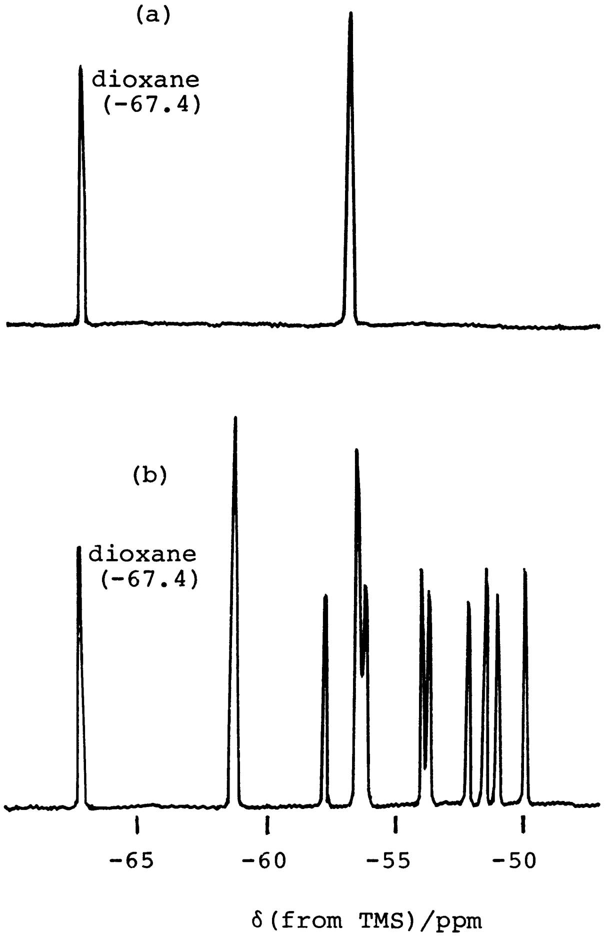


Fig. 3 ^{13}C NMR spectra of the isomers $[Co(hexaen)]^{3+}$ in 0.01 M HCl at 35 °C.

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REFERENCES AND NOTE

1) Y. Yoshikawa, *Bull. Chem. Soc. Jpn.*, 49, 159(1976).
2) Y. Yoshikawa, M. Kojima, and K. Yamasāki, Presented at the annual meeting of the Chemical Society of Japan, April, 1975.
3) M. Kojima, M. Iwagaki, Y. Yoshikawa, and J. Fujita, *Bull. Chem. Soc. Jpn.*, 50, 3216(1977).
4) The meso isomer was named "Cobalt Spinner" after a spinning wheel.

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