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Isomerism of the Metal Complexes Containing Multidentate Ligands. VII.[1] The Conformational Analysis of the Isomers of $[Co(linpen)]^{3+}$ *

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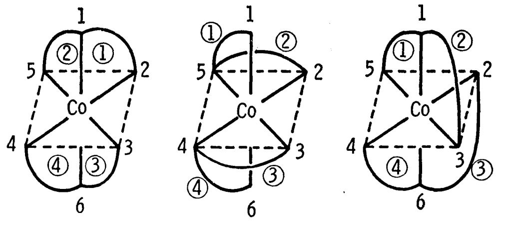
The conformational analysis of the $[Co(dien)_2]^{3+}$ and $[Co(linpen)]^{3+}$ (dien=$H_2N(CH_2CH_2NH)_2H$, linpen=$H_2N(CH_2CH_2NH)_5H$) complexes has been carried out. The former, which can exist in three geometric isomers, was selected as a standard for the determination of several parameters in the strain-energy calculation; they were determined so that the calculated geometries of these isomers were almost the same as those obtained from the crystal structure analysis studies. These results were applied to the strain-energy calculation for the latter, $[Co(linpen)]^{3+}$, which can exist in four geometric isomers. Further, in three of these isomers, some conformational isomers are possible. From the results of the energy-minimized conformational-analysis calculations of these isomers, it has turned out that the assignment of the structures of the configurational and conformational isomers is possible.

A conformational analysis technique has been effectively used to obtain information about the conformational structures of molecules. The strain-energy-minimization technique developed by Boyd[2] has been very frequently applied not only to organic molecules, but also to metal complexes.

Recently Toriumi and Saito[3] modified Boyd's method and reported the results of:

$(+)_{589}$*cis*-β-$[Co(CO_3)(S,S\text{-}3,8\text{-dimetrien})]^{+}$[4] calculated by it.

In the present study we have adopted the method of Toriumi and Saito, the main part of which is the same as Boyd's, and calculated the strain energies of the isomers of $[Co(dien)_2]^{3+}$ and $[Co(linpen)]^{3+}$. The force field in this calculation includes contributions from bond stretching, nonbonded interactions, angle bending, and torsional potentials. In the calculations of the nonbonded interactions, only those between nonbonded atoms (except between atoms bonded to the same atom) up to distances of 1.2 times the sum of each van der Waas radius (1.50 Å for N, 1.55 Å for C and 1.20 Å for H atoms) have been treated; the interactions containing a cobalt atom have been omitted. The purpose of this study is to investigate the details of the molecular structures of $[Co(linpen)]^{3+}$ isomers, the isolation and characterization of which have already been reported in this Bulletin.[5] We will first carry out a conformational analysis of the isomers of $[Co(dien)_2]^{3+}$ in order to determine the adequate parameters in the calculation of strain energies by comparing the energy-minimized structures with those determined by X-ray studies.



s-fac *u-fac* *mer*

Fig. 1. Three possible geometric isomers of $[Co(dien)_2]^{3+}$. Figures in the circles show the numberings for the chelate rings.

The complex ion, $[Co(dien)_2]^{3+}$, can exist in three geometric isomers, as Fig. 1 shows, and they have all been isolated.[6] Saito *et al.* determined the molecular structures of *s-facial* and *u-facial* isomers of $[Co(dien)_2]^{3+}$ by the X-ray crystal analysis of *s-fac*-$[Co(dien)_2]Br_3$[7] and $\{-\}_{502}$*u-fac*-$[Co(dien)_2][Co(CN)_6]\cdot 2H_2O$**,[8] respectively. According to these results, *s-fac*-$[Co(dien)_2]^{3+}$ has approximately the C_{2h} symmetry and $\{-\}_{502}$*u-fac*-$[Co(dien)_2]^{3+}$ (there are two conformational isomers in the crystals of this complex hexacyanocobaltate(III)), the C_2 symmetry. The conformations of the four

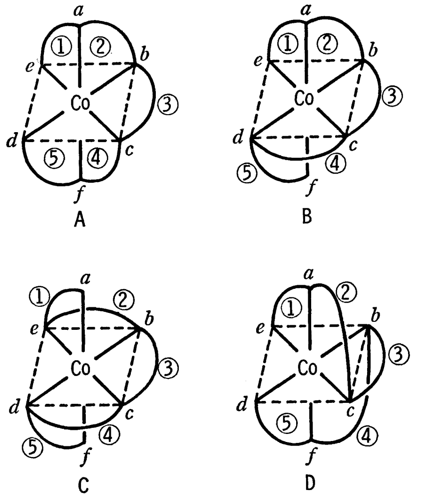


Fig. 2. Four possible geometric isomers of $[Co(linpen)]^{3+}$. Letters, *a*—*f*, are the locant designators according to the nomenclature proposed by IUPAC.[9]

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** The $\{+\}_\lambda$ or $\{-\}_\lambda$ symbol represents the sign of the CD spectrum at a certain wavelength, λ nm, and $\{-\}_{502}$ corresponds to $(-)_{589}$ in the *u-fac*-$[Co(dien)_2]^{3+}$ complex. This symbol is convenient for characterizing an optically active compound, because there is no need to measure an optical rotation. For the λ, wavelength, it is advisable to adopt that of a maximum CD intensity in a suitable band.

chelate rings in the former are $\lambda\delta\lambda\delta$ (or $\delta\lambda\delta\lambda$), in the order of the numbers of the chelate rings in Fig. 1, while those of the latter are $\lambda\delta\delta\lambda$ and $\lambda\lambda\lambda\lambda$ (denoted as *u-fac*-1 and *u-fac*-2 respectively) for the determined absolute configuration, that is to say, they are skew chelate pairs $\Delta\Lambda\Delta$ (Fig. 1). On the other hand, the structure of *mer*-$[Co(dien)_2]^{3+}$ has not yet been determined. However, it is expected to have a two-fold axis.

The linpen ligand consists of two dien linearly linked by an ethylene group ($-CH_2CH_2-$) between the individual primary amine-N atoms. Therefore, the structures of $[Co(linpen)]^{3+}$, which can exist in four different configurational isomers (Fig. 2), are closely related to those of $[Co(dien)_2]^{3+}$. For example, the A and C isomers are formed by linking N2 to N3 by an ethylene group in the *s-facial* and *u-facial* isomers respectively.

Results and Discussion

The Conformational Analysis of the Isomers of $[Co(dien)_2]^{3+}$. Dwyer *et al.* have attempted the conformational analysis of $[Co(dien)_2]^{3+}$ isomers by using the strain-energy-minimization technique.[10] We analyzed these isomers independently.

The initial molecular structure of each isomer was constructed from the internuclear bond distances; Co–N (primary amine): 1.97 Å, Co–N (secondary amine): 1.95 Å, N–C: 1.49 Å, C–C: 1.51 Å, N–H: 1.03 Å, and C–H: 1.09 Å; the valency angles, ∠NCoN (chelate ring): 86.0°, ∠CoNC: 105—114°, ∠NCC: 105—114°, ∠CNC: 106—118° (*facial*) and 121° (*meridional*), and the angles related to H atoms: 109.5°. Their strain-energy-minimizations were carried out for several sets of equilibrium internuclear bond distances, Co–N, N–C, and C–C, the other parameters[11] being kept constant. Consequently, it was found to be adequate to use the values of 1.935, 1.485, and 1.51 Å for the Co–N, N–C, and C–C equilibrium bond distances respectively, for better fitting the resulting molecular structures to those obtained by X-ray methods. The energy terms obtained from these minimizations, where the root-mean-square coordinate deviations are smaller than 0.005 Å, are shown in Table 1. There are not large differences among these total energies.

Table 1. Final energy terms for the isomers of $[Co(dien)_2]^{3+}$

Isomer	Bond	Nonbond	Angle	Torsion	Total	
s-fac	0.19	1.45	0.55	1.88	4.08	kJ/mol
u-fac-1	0.20	1.46	0.57	1.89	4.12	
u-fac-2	0.26	1.49	0.67	1.70	4.12	
mer	0.26	1.22	1.30	1.29	4.06	

On the other hand, the formation ratios found experimentally in the equilibrium mixture of bromides (25 °C) were *s-fac*: *u-fac*: *mer*=7: 30: 63.

Therefore, the correlation between the minimized strain-energy and the formation percentage of each isomer is not necessarily good. In this case, there may be an inadequate choice for any parameters in the minimization and/or zero level imbalances.[10] The presently calculated molecular geometries (Table 2) are, nevertheless, presumed to be sufficiently accurate by comparison with the experimental structures. Some of these values will be used to construct the molecular structures of $[Co(linpen)]^{3+}$ isomers in the next section.

The Conformational Analysis of the Isomers of $[Co(linpen)]^{3+}$. Figure 2 shows the four geometric isomers of $[Co(linpen)]^{3+}$. The A structure has only secondary amine; the >NH groups of its facial structure are formed in *facial* isomers of $[Co(dien)_2]^{3+}$, but none of the meridional structure. Therefore, this is represented by f_4.*** The B structure contains one >NH group of the meridional structure and is represented by f_2mf (or fmf_2).*** Both the C and D structures have two >NH groups of each structure; they are represented by fm_2f and mf_2m*** respectively.

When the absolute configurations around the secondary amine-N atoms are taken into account for each structure in Fig. 2, the number of isomers is 1 (f_4-*RSSR*=I) for the A, 2 each (f_2mf-*RSRS*, -*RSSS*=II-1, II-2 and fm_2f-*SRRS*, -*SSSS*=III, IV) for B and C respectively, and 3 (mf_2m-*RRRR*, -*RRRS*, -*SRRS*=V, VI, VII) for the D structure, making a total of 8, where *R* and *S*

Table 2. Molecular geometries of the isomers of $[Co(dien)_2]^{3+}$

	$Co-NH_2$[a)] Co–NH	$C-NH_2$[a)] C–NH	C–C[a)]	∠NCoN Chelate ring	∠CNC[a)]
s-fac	1.966Å (1.97Å)[b)]	1.491Å (1.48Å)	1.515Å (1.51Å)	88.3—88.9°(86.6—87.2°)	113.8°(116.0°)
	1.944 (1.95)	1.494 (1.505)			
u-fac-1	$\left\{\begin{matrix}1.958\\1.968\end{matrix}\right\}\left(\left\{\begin{matrix}1.957\\1.969\end{matrix}\right\}\right)$	1.490 (1.491)	1.513 (1.516)	87.0—88.3 (85.4—86.4)	113.0 (113.9)
	1.960 (1.970)	1.495 (1.496)			
u-fac-2	$\left\{\begin{matrix}1.952\\1.973\end{matrix}\right\}\left(\left\{\begin{matrix}1.951\\1.968\end{matrix}\right\}\right)$	1.488 (1.488)	1.514 (1.509)	86.8—87.0 (84.9—85.7)	110.3 (110.4)
	1.971 (1.970)	1.497 (1.499)			
mer	1.976	1.495	1.514	86.0—86.1	114.5
	1.942	1.486			

a) Averages of corresponding values are given. b) Figures in parentheses are the values determined from X-ray crystal structure analysis.[7,8)]

*** These designations, f_4, f_2mf, fm_2f, and mf_2m, can be represented by *acbfed*, *acbfde*, *aebcdf*, and *acfbed* respectively by the use of the locant designators according to the nomenclature proposed by IUPAC.[9)] The former can also be used as such for optical isomers the absolute configurations of which are not known.

represent the absolute configurations around the secondary amine-N atoms; they are written in the same order as that of *f* and *m*. These eight isomers (I, II-1, II-2, III—VII) have actually been found by means of column chromatography on SP-Sephadex and thus characterized.[5] The II-1 and II-2 isomers, however, were labile and isomerized into a mixture with the formation ratio of about 1: 1 during the isolation, so they could not be obtained in pure states. All the isomers have the corresponding catoptric forms. In the calculation, the catoptromers shown in Fig. 2 were used. The averages of the individual geometrical values based upon the minimum strain energies of the [Co(dien)$_2$]$^{3+}$ isomers were mainly used to construct the initial molecular structures of [Co(linpen)]$^{3+}$ isomers with the corresponding ones. In this case, the valency angles, ∠CNC, were 110—114° for the facial and 115—122° for the meridional structures. The force constants and the other parameters in the minimization were the same as for the isomers of [Co(dien)$_2$]$^{3+}$.

The highest symmetries for *f*$_4$-*RSSR*, *fm*$_2$*f*-*SRRS*, -*SSSS*, *mf*$_2$*m*-*RRRR*, and -*SRRS* are C$_2$, so the calculations for these isomers were initiated from the structures with C$_2$ symmetry, whereas the *f*$_2$*mf*-*RSRS*, -*RSSS*, and *mf*$_2$*m*-*RRRS* isomers possess only the C$_1$ symmetry. In the course of the minimization, the symmetry of each isomer was not considered, but all the isomers possessing C$_2$ symmetry except for *f*$_4$-*RSSR* were energy-minimized retaining this symmetry, within the limits of error. The symmetry of the energy-minimized structure of the *f*$_4$-*RSSR* isomer was C$_1$, and its energy was smaller than that of the structure the C$_2$ symmetry of which was retained in the course of the minimization. The final energy terms are presented in Table 3. All the terms coordinate deviations were smaller than 0.005 Å. The formation percentages in Table 3 are those in the equilibrium mixture of chlorides (25 °C). The III and IV isomers were assigned to *fm*$_2$*f*-*SRRS* and -*SSSS* for the first time on the basis of these results. As a whole, there is a rough tendency for the isomer of a large percentage to have a low minimized energy. When the data in Table 3 are plotted, with the minimized energy as the ordinate and the logarithm of the formation percentage as the abscissa, a very rough linear relationship is obtained (Fig. 3).

If the conformational structure (δ, λ) of each chelate ring is not taken into consideration, only the *f*$_2$*mf* II-1 and II-2 isomers have the C$_1$ symmetry, while all the others have the C$_2$ symmetry. Therefore, the former are favored by a statistical factor of two over the latter; those formation percentages were divided by two when their data were plotted in Fig. 3. The relatively high abundances of the VI and VII isomers, when considered with their energies, may account for the conformational equilibria being almost independent of those among the configurational isomers; that is to say, the very high stability of the V isomer may make the VI and VII isomers form more abundantly. These results show that conformational analysis may be a technique for the assignment of the structures of the configurational isomers.

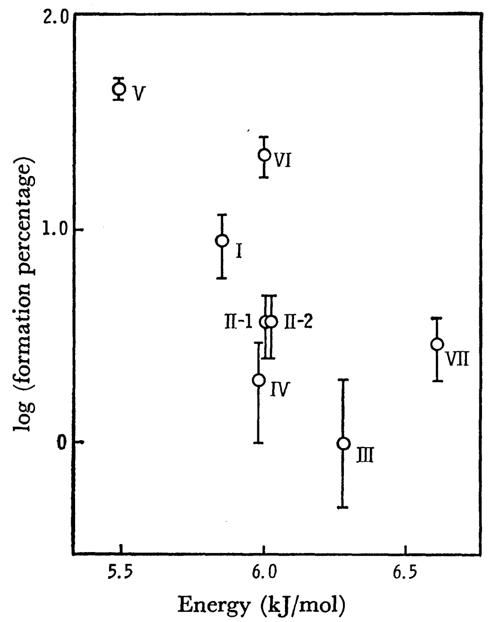

Fig. 3. Plot of log(formation percentage) *vs.* minimized energy for the isomers of [Co(linpen)]$^{3+}$. The formation percentages of both the II-1 and II-2 isomers were divided by two because of the statistical preference for these structures.

In all the calculations described here, the complexes are dealt with as free molecules. In practice, however, they have some mutual interactions with their surroundings. Therefore, it is an important problem awaiting solution to take into account these effects in order to obtain more accurate energies.

All the molecular geometries obtained by the method of the conformational analysis are presented in Table 4.

Table 3. Final energy terms for the isomers of [Co(linpen)]$^{3+}$ (Fig. 2)

Isomer	Sign of CD	Absolute configuration	Proposed[a)] prefix	Bond	Nonbond	Angle	Torsion	Total		Formation percentage
I	$\{+\}_{502}$	$\Lambda\Lambda\Lambda\Delta$	*f*$_4$-*RSSR*	0.33	2.22	0.86	2.45	5.85	kJ/mol	9%
II-1	$\{+\}_{492}$	$\Lambda\Lambda\Lambda\Lambda\Delta$	*f*$_2$*mf*-*RSRS*	0.32	2.04	1.33	2.34	6.02		15
II-2	$\{+\}_{492}$	$\Lambda\Lambda\Lambda\Lambda\Delta$	*f*$_2$*mf*-*RSSS*	0.35	2.08	1.30	2.27	6.00		
III	$\{+\}_{485}$	$\Lambda\Lambda\Lambda\Delta\Delta$	*fm*$_2$*f*-*SRRS*	0.32	1.71	2.28	1.97	6.28		1
IV	$\{+\}_{453}$	$\Lambda\Lambda\Lambda\Delta\Delta$	*fm*$_2$*f*-*SSSS*	0.32	1.82	1.97	1.87	5.98		2
V	$\{+\}_{475}$	$\Lambda\Lambda\Lambda\Lambda\Delta\Delta$	*mf*$_2$*m*-*RRRR*	0.33	1.79	1.30	2.06	5.48		47
VI	$\{+\}_{469}$	$\Lambda\Lambda\Lambda\Lambda\Delta\Delta$	*mf*$_2$*m*-*RRRS*	0.38	1.84	1.89	1.89	5.99		23
VII	$\{+\}_{469}$	$\Lambda\Lambda\Lambda\Lambda\Delta\Delta$	*mf*$_2$*m*-*SRRS*	0.42	2.06	2.23	1.90	6.60		3

a) For example, the full designation for the isomer, $\{+\}_{502}$ I is $\Lambda\Lambda\Lambda\Delta$-*f*$_4$(*RSSR*)-[Co(linpen)δλδλδ]$^{3+}$, where the last small Greek letters show the conformations of chelate rings from one end to the other.

Table 4. Molecular geometries of the isomers of $[Co(linpen)]^{3+}$ (Fig. 2)

Isomer	Bond length Co–N					
	N(*a*)	N(*b*)	N(*c*)	N(*d*)	N(*e*)	N(*f*)
I, f_4-*RSSR*	1.958	1.967	1.973	1.971	1.974	1.969 Å
I, f_4-*RSSR**	1.963	1.968	1.972	1.973	1.975	1.970
II-1, f_2mf-*RSRS*	1.965	1.961	1.952	1.970	1.977	1.975
II-2, f_2mf-*RSSS*	1.983	1.964	1.948	1.974	1.976	1.966
III, fm_2f-*SRRS*	1.982	1.943	1.943	1.963	1.963	1.982
IV, fm_2f-*SSSS*	1.980	1.936	1.937	1.958	1.958	1.981
V, mf_2m-*RRRR*	1.947	1.969	1.969	1.982	1.982	1.947
VI, mf_2m-*RRRS*	1.953	1.986	1.974	1.974	1.985	1.947
VII, mf_2m-*SRRS*	1.953	1.990	1.991	1.978	1.978	1.952

Isomer	Valence angle ∠NCoN chelate ring				
	1	2	3	4	5
I, f_4-*RSSR*	87.2	88.6	86.9	87.1	86.1°
I, f_4-*RSSR**	86.9	88.2	87.1	87.3	86.1
II-1, f_2mf-*RSRS*	85.3	89.3	84.9	87.0	86.8
II-2, f_2mf-*RSSS*	85.2	87.4	86.7	84.5	88.2
III, fm_2f-*SRRS*	85.0	87.5	86.3	87.5	85.0
IV, fm_2f-*SSSS*	88.1	86.8	87.3	86.8	88.0
V, mf_2m-*RRRR*	85.7	85.0	89.0	85.0	85.7
VI, mf_2m-*RRRS*	84.6	84.9	87.3	85.8	85.5
VII, mf_2m-*SRRS*	84.0	85.8	86.1	85.8	84.0

Isomer	Dihedral angle ∠NCCN[a)] chelate ring				
	1	2	3	4	5
I, f_4-*RSSR*	+43.4	−39.4	+41.7	−41.5	+39.0°
I, f_4-*RSSR**	+42.5	−40.1	+41.5	−41.7	+39.2
II-1, f_2mf-*RSRS*	+38.9	−46.1	−37.1	+46.6	−40.6
II-2, f_2mf-*RSSS*	+41.0	−40.6	+45.8	−35.1	−49.2
III, fm_2f-*SRRS*	−41.7	+44.0	−52.4	+44.1	−41.7
IV, fm_2f-*SSSS*	−50.2	−39.0	+53.0	−39.0	−49.7
V, mf_2m-*RRRR*	+48.6	−36.4	−52.2	−36.5	+48.7
VI, mf_2m-*RRRS*	−47.6	−37.0	−47.2	+44.5	+49.6
VII, mf_2m-*SRRS*	−44.5	+47.4	−40.7	+47.4	−44.4

a) Positive and negative signs represent δ and λ conformations of chelate rings, respectively.

* As the initial molecular coordinates, those from the X-ray analysis[12)] were used.

Generally, the Co–N bond lengths are 1.97—1.98 Å for primary amines, and 1.96—1.97 and 1.94—1.95 Å for secondary amines, with facial and meridional structures respectively, except for a part of the II-2, VI, and VII isomers. The valency angles, ∠NCoN (chelate ring), in the meridional structure are smaller than those in the facial structure.

As the I isomer contains only the facial structure, it can be predicted that the strain for the valency angles in this isomer is smaller than those in all the others which contain the meridional structures; this is in accord with the result shown in Table 3. On the other hand, the III—VII isomers, which contain two meridional structures, have appreciably large strains for all the valency angles except for the V isomer. The strain of the V isomer may be moderately released at the sacrifice of that for the torsion.

During the course of the present study, Sato and Saito have determined the molecular structure of the $\{+\}_{502}$I isomer from an X-ray analysis of $\{+\}_{502}[Co(linpen)][Co(CN)_6]\cdot 3H_2O$.[12)] The structure which we predicted and energy-minimized agreed completely in its conformations and configurations with that determined by them.

We also carried out the minimization for the I isomer by using the molecular coordinates obtained from the X-ray analysis[12)] as the initial ones. These results are also included in Table 4. The agreement between this structure and that obtained previously is excellent.

Thus, we can obtain accurate information on the molecular structures of cobalt(III) complexes from the energy-minimized conformational analysis calculation.

We wish to thank Mr. Koshiro Toriumi and Professor Yoshihiko Saito of the Institute for Solid State Physics, the University of Tokyo, for the permission to use their computer programs and for their valuable discussions. Mr. Koshiro Toriumi also provided helpful advice. We are also indebted to Professors Shoichi Sato and Yoshihiko Saito for obtaining the X-ray crystal analysis data on the $\{+\}_{502}$I isomer of $[Co(linpen)]^{3+}$. Thanks are also due to the Nagoya University Computer Center for the use of the FACOM 230-60 computer. This research was supported in part by the Matsunaga Science Foundation.

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