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Studies of the Metal Complexes of Cyclohexane Derivatives. IX.[1] The Preparation and Properties of Platinum(II) Complexes Containing Methyl Derivatives of *cis*-1,2-Cyclohexanediamine

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Four 1,2-diamine ligands, (1*RS*,2*SR*)-1-methyl-1,2-cyclohexanediamine(1m-chxn), (1*R*,2*S*,3*R*)-3-methyl-1,2-cyclohexanediamine(*R,S,R*-3m-chxn), (1*S*,2*R*,4*R*)-4-methyl-1,2-cyclohexanediamine(*S,R,R*-4m-chxn), and (1*R*,2*S*,4*R*)-4-methyl-1,2-cyclohexanediamine(*R,S,R*-4m-chxn), were prepared. The mixed-ligand complexes of the $[PtXL]^{2+}$ type (X=$(NH_3)_2$, 1,2-ethanediamine, *meso*-2,3-butanediamine, and 2,3-dimethyl-2,3-butanediamine, L=each m-chxn) were synthesized and characterized by means of their electronic, circular dichroism, and ^{13}C NMR spectra. The chelate ring formed by *S,R,R*-4m-chxn was almost conformationally fixed to take a δ conformation, while the chelate rings of 1m-chxn, *R,S,R*-3m-chxn, and *R,S,R*-4m-chxn easily interchange between δ and λ conformations. The stereochemistries of these three complexes are attributable to the conformational requirements for both the cyclohexane ring and the chelate ring, for which synchronous inversions are presumed.

The conformations of chelate rings of C-substituted 1,2-diamine complexes in solution have been extensively studied. Most of them may be classified into two types.

(1) In the complexes containing a chelate ligand with achiral carbon atoms or enantiotopic carbon atoms[2] in its chelate ring, such as 2,3-dimethyl-2,3-butanediamine(dmbn) and *meso*-2,3-butanediamine(*m*-bn), the distributions of the two conformations in the $\delta \rightleftarrows \lambda$ equilibrium are equal as a result of the rapid interconversion.[3-5]

(2) In the complexes containing a chelate ligand with one chiral carbon atom or two diastereotopic carbon atoms,[2] such as (2*R* or 2*S*)-1,2-propanediamine and (2*R*,3*R* or 2*S*,3*S*)-2,3-butanediamine, the chelate rings take predominantly either a δ or a λ conformation.[3-5] However, the complexes formed by the other type of 1,2-diamine, which has an unsymmetrical structure due to constitutionally nonequivalent substituents attached to the chelate ring carbon atom(s), have not been so widely investigated.

Recently we have reported on the preparation and properties of the complexes containing the latter type of ligand, 1-aminomethyl-2-methylcyclohexylamine[6] or (1*R*,2*S*,3*S* or 1*S*, 2*R*,3*R*)-3-methyl-1,2-cyclohexanediamine (*R,S,S*- or *S,R,R*-3m-chxn).[1] In these complexs, the conformations of the chelate ring are almost fixed by means of the steric effect of the methyl group attached to the carbon atom outside the chelate ring. As an extention of these earlier studies, we have now synthesized some Pt^{II} complexes containing four new diamines (m-chxn), (1*RS*,2*SR*)-1-methyl-1,2-cyclohexanediamine(1m-chxn), (1*R*,2*S*,3*R*)-3-methyl-1,2-cyclohexanediamine(*R,S,R*-3m-chxn), (1*S*,2*R*,4*R*)-4-methyl-1,2-cyclohexanediamine(*S,R,R*-4m-chxn), and (1*R*,2*S*,4*R*)-4-methyl-1,2-cyclohexanediamine(*R,S,R*-4m-chxn). In this paper, the conformations of the m-chxn chelate rings will be discussed on the basis of the platinum–carbon coupling constants in the ^{13}C NMR spectra.

Experimental

Preparation of the Ligands. (1*RS*,2*SR*)-1-Methyl-1,2-cyclohexanediamine(1m-chxn): 1-Methyl-*r*-1,*c*-2-cyclohexanedicarboxylic acid was synthesized from butadiene and citraconic anhydride according to the literature.[7] From this acid, 1m-chxn was prepared by a method similar to that reported by Werner.[8] It was purified as the dihydrochloride. Found: C, 41.52; H, 8.99; N, 13.69%. Calcd for $C_7H_{16}N_2 \cdot 2HCl$: C, 41.80; H, 9.02; N, 13.93%.

(1*R*,2*S*,3*R*)-3-Methyl-1,2-cyclohexanediamine(*R,S,R*-3m-chxn): *t*-3-Methyl-*r*-1,*c*-2-cyclohexanedicarboxylic acid was obtained by a manner similar to that described in the literature.[9] (1*RS*,2*SR*,3*RS*)-3m-chxn was prepared by the same procedure as 1m-chxn. It was optically resolved using (2*R*,3*R*)-di-*O*-benzoyltartaric acid. The less soluble benzoyltartrate obtained, whose optical rotation could not be measured because of its low solubility, was recrystallized twice from EtOH–H_2O (1:2). Mp(decomp) 205—206 °C. Anal. ($C_{25}H_{30}N_2O_8$) C, H, N. By treating this salt with a 3 mol dm^{-3} HCl solution, *R,S,R*-3m-chxn·2HCl was obtained. Found: C, 42.11; H, 9.18; N, 13.63%. Calcd for $C_7H_{16}N_2 \cdot 2HCl$: C, 41.80; H, 9.02; N, 13.93%. $[\alpha]_D = -33.8°$ (*c* 2.0, H_2O). The assignments of the absolute configurations of the three optically active diamines studied in this paper will be described in a later section.

(1*S*,2*R*,4*R*)- and (1*R*,2*S*,4*R*)-4-Methyl-1,2-cyclohexanediamine (*S,R,R*- and *R,S,R*-4m-chxn): Commercially available 4-methyl-1,2-cyclohexanedicarboxylic anhydride (Aldrich Co., Ltd.) was hydrolyzed. A white powder(**A**) was obtained nearly quantitatively; mp(decomp) 161—171 °C. A suspension of 270 g of **A** in 480 cm^3 of 2-propanol was heated to bp and then cooled. A white powder (**B**, 150 g) was thus obtained; mp(decomp) 179—180 °C. This was recrystallized twice from 2-propanol to give 48 g of acid **C**; mp(decomp) 185—186 °C. This acid was *t*-4-methyl-*r*-1,*c*-2-cyclohexanedicarboxylic acid contaminated by a very small amount of the *c,c*-isomer. This contaminant could be removed during the course of optical resolution. To the

filtrate obtained after removing **B**, an excess amount of an aqueous ammonia solution was added. The resulting mixture was evaporated to dryness to yield 65 g of a crude mixture of monoammonium salt of *c,c*- and *t,c*-acid. This was recrystallized from EtOH–H_2O (1:2) to give 57 g of crystals. Treating this salt with a 3 mol dm^{-3} HCl solution gave 49 g of pure *c*-4-methyl-*r*-1,*c*-2-cyclohexanedicarboxylic acid(**D**; mp(decomp) 171—172 °C).

From acid **D**, 1*SR*,2*RS*,4*RS*-4m-chxn was prepared by the same manner as was used for the synthesis of 1m-chxn and *R,S,R*-3m-chxn. This was optically resolved by the use of (2*R*,3*R*)-di-*O*-benzoyltartaric acid. The less soluble benzoyltartrate was recrystallized from EtOH–H_2O (1:2). Anal. ($C_{25}H_{30}N_2O_8 \cdot H_2O$) C, H, N. $[\alpha]_D = -68.6°$ (*c* 1.0, MeOH). Treating this salt with a 3 mol dm^{-3} HCl solution gave *S,R,R*-4m-chxn·2HCl. Found: C, 41.44; H, 9.04; N, 13.91%. Calcd for $C_7H_{16}N_2 \cdot 2HCl$: C, 41.80; H, 9.02; N, 13.93%. $[\alpha]_D = +23.0°$ (*c* 2.0, H_2O).

The *R,S,R*-4m-chxn compound was prepared from acid **C** by a similar Schmidt reaction.[8] It was optically resolved using the same resolving reagent as was used for *S,R,R*-4m-chxn. The less soluble diastereomeric salt obtained was recrystallized twice from H_2O–DMF (2:1); mp(decomp) 174—175 °C. Anal. ($C_{25}H_{30}N_2O_8 \cdot 2H_2O$) C, H, N. $[\alpha]_D = -72°$ (*c* 0.5, MeOH). From this tartrate, *R,S,R*-4m-chxn·2HCl was obtained by a usual work up. Found: C, 42.05; H, 8.91; N, 13.87%. Calcd for $C_7H_{16}N_2 \cdot 2HCl$: C, 41.80; H, 9.02; N, 13.93%. $[\alpha]_D = +21.2°$ (*c* 2.1, H_2O).

Preparation of Complexes. $[Pt(NH_3)_2L]Cl_2$ (L= each m-chxn): These complexes were prepared by the reaction of $[PtCl_2L]$[10] with aqueous ammonia. Found: $[Pt(NH_3)_2$(1m-chxn)$]Cl_2 \cdot 0.5H_2O$, C, 19.00; H, 5.36; N, 12.74%. $[Pt(NH_3)_2$(*R,S,R*-3m-chxn)$]Cl_2 \cdot 0.5H_2O$, C, 19.11; H, 5.51; N, 12.98%. Calcd for $C_7H_{23}N_4O_{0.5}Cl_2Pt$: C, 19.23; H, 5.30; N, 12.81%. Found: $[Pt(NH_3)_2$(*S,R,R*-4m-chxn)$]Cl_2 \cdot H_2O$, C, 18.94; H, 5.35; N, 12.61%. Calcd for $C_7H_{24}N_4OCl_2Pt$: C, 18.84; H, 5.42; N, 12.55%. Found: $[Pt(NH_3)_2$(*R,S,R*-4m-chxn)$]Cl_2$, C, 19.61; H, 5.01; N, 12.92%. Calcd for $C_7H_{22}N_4Cl_2Pt$: C, 19.63; H, 5.18; N, 13.08%.

[Pt(en)L]Cl_2: These complexes were prepared by the reaction of $[PtCl_2(en)]$[11] with L in water. The aqueous solution of L was obtained from the m-chxn·2HCl solution by passing it through an anion-exchange resin column (Dowex, 1-X8, OH^- form). Found: [Pt(en)(1m-chxn)]-$Cl_2 \cdot 0.5H_2O$, C, 23.47; H, 5.28; N, 11.61%. [Pt(en)(*R,S,R*-3m-chxn)$]Cl_2 \cdot 0.5H_2O$, C, 23.00; H, 5.58; N, 12.15%. Calcd for $C_9H_{25}N_4O_{0.5}Cl_2Pt$: C, 23.33; H, 5.44; N, 12.09%. Found: [Pt(en)(*S,R,R*-4m-chxn)$]Cl_2$, C, 23.69; H, 5.22; N, 12.39%. [Pt(en)(*R,S,R*-4m-chxn)$]Cl_2$, C, 23.92; H, 5.26; N, 11.96%. Calcd for $C_9H_{24}N_4Cl_2Pt$: C, 23.79; H, 5.33; N, 12.33%.

[Pt(*m*-bn)L]Cl_2: The *m*-bn ligand was synthesized by a literature method.[12] The complexes were synthesized in a way similar to that used for the preparation of $[Pt(en)L]Cl_2$. Found: [Pt(*m*-bn)(1m-chxn)$]Cl_2$, C, 27.30; H, 5.79; N, 11.42%. [Pt(*m*-bn)(*S,R,R*-4m-chxn)$]Cl_2$, C, 27.39; H, 5.99; N, 11.93%. Calcd for $C_{11}H_{28}N_4Cl_2Pt$: C, 27.39; H, 5.85; N, 11.62%. [Pt(*m*-bn)(*R,S,R*-3m-chxn)$]Cl_2 \cdot 0.5H_2O$, C, 26.83; H, 5.93; N, 11.52%. [Pt(*m*-bn)(*R,S,R*-4m-chxn)$]Cl_2 \cdot 0.5H_2O$, C, 26.94; H, 5.89; N, 11.66%. Calcd for $C_{11}H_{29}N_4O_{0.5}Cl_2Pt$: C, 26.89; H, 5.95; N, 11.40%.

[Pt(dmbn)L]Cl_2: The dmbn ligand was prepared by the known procedure.[13] The complexes were obtained by the reaction of $[PtCl_2L]$ with an aqueous solution of dmbn. Found: [Pt(dmbn)(1m-chxn)$]Cl_2 \cdot 1.5H_2O$, C, 29.21; H, 6.34; N, 10.45%. [Pt(dmbn)(*R,S,R*-3m-chxn)$]Cl_2 \cdot 1.5H_2O$, C, 28.91; H, 6.47; N, 10.34%. [Pt(dmbn)(*S,R,R*-4m-chxn)$]Cl_2 \cdot 1.5H_2O$, C, 29.23; H, 6.47; N, 10.56%. Cacld for $C_{13}H_{35}N_4O_{1.5}Cl_2Pt$: C, 29.05; H, 6.56; N, 10.42%. Found: [Pt(dmbn)-(*R,S,R*-4m-chxn)$]Cl_2 \cdot H_2O$, C, 29.67; H, 6.55; N, 11.27%. Calcd for $C_{13}H_{34}N_4OCl_2Pt$: C, 29.55; H, 6.49; N, 10.60%.

Measurements. The CD and electronic spectra were measured using a JASCO J-40 spectropolarimeter and a Shimadzu UV-210-A spectrometer respectively. The optical rotations were measured with a JASCO DIP-4 polarimeter. The ^{13}C NMR spectra were recorded on a JEOL JNM-FX-100 spectrometer using D_2O as a solvent. The chemical shifts were reported relative to the dioxane (δ 67.70) added as an internal reference. The measurements of all the complexes except for the *R,S,R*-4m-chxn complexes were recorded with 8 K data points. For the *R,S,R*-4m-chxn complexes, the measurements were run with 16 K data words. The ^{13}C NMR spectra of some of the complexes, which were not sufficiently soluble in D_2O, were recorded after converting their counter anions to F^-.

Results and Discussion

Preparation of the Ligands. The diamines were

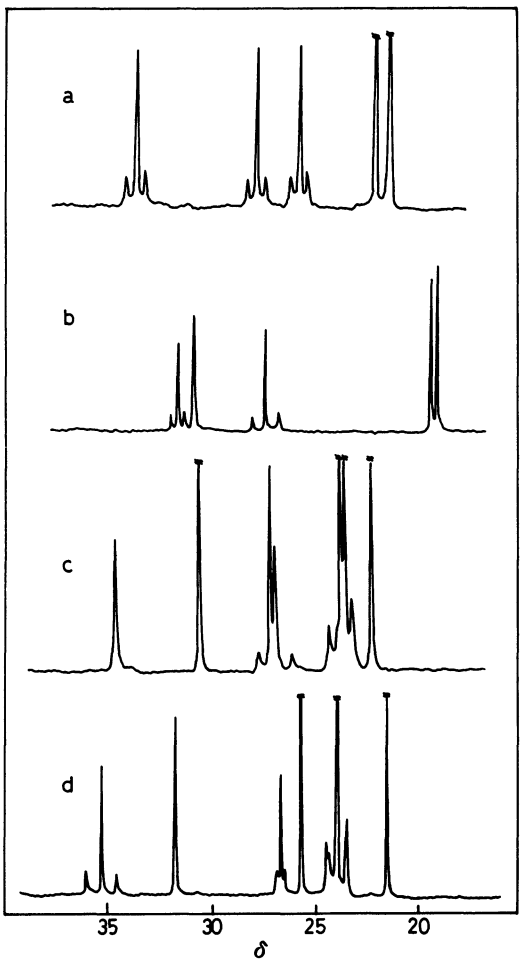


Fig. 1. ^{13}C NMR Spectra of $[Pt(NH_3)_2$(1m-chxn)$]Cl_2$ (a), $[Pt(NH_3)_2$(*R,S,R*-3m-chxn)$]Cl_2$ (b), [Pt(dmbn)-(*S,R,R*-4m-chxn)$]Cl_2$ (c), and [Pt(dmbn)(*R,S,R*-4m-chxn)$]Cl_2$ (d).

Table 1. ^{13}C NMR Chemical Shifts[a] and Coupling Constants[b] for $[PtX(m\text{-chxn})]^{2+}$

Complex	m-chxn								X		
	α-Carbon		β-Carbon			Other carbon					
	(C_1, C_2)		C_3	C_6	CH_3	(C_4, C_5)		CH_3			
$[Pt(NH_3)_2(1m\text{-chxn})]^{2+}$	62.83	62.58	27.83 (22.0)	33.78 (23.2)	25.74 (20.8)	22.03	21.30	—			
$[Pt(en)(1m\text{-chxn})]^{2+}$	62.24	62.00	27.79 (20.8)	33.78 (23.2)	25.74 (20.8)	22.03	21.25	—	47.91		
$[Pt(m\text{-bn})(1m\text{-chxn})]^{2+}$	62.19	62.10	27.79 (19.5)	33.83 (23.2)	25.79 (20.8)	22.13	21.25	—	57.56	57.47	14.14 14.04 (25.6)
$[Pt(dmbn)(1m\text{-chxn})]^{2+}$	62.14	61.95	27.79 (19.5)	33.78 (23.2)	25.74 (20.8)	22.08	21.25	—	64.29		23.79 (23.2)
$[Pt(NH_3)_2(R,S,R\text{-}3m\text{-chxn})]^{2+}$	64.68 (7)	57.90	31.68 (18.3)	27.40 (33.0)	—	30.86	19.26	19.01			
$[Pt(en)(R,S,R\text{-}3m\text{-chxn})]^{2+}$	64.24 (9)	57.47	31.73 (18.3)	27.40 (33.0)	—	30.95	19.26	18.96	48.01	47.86	
$[Pt(m\text{-bn})(R,S,R\text{-}3m\text{-chxn})]^{2+}$	64.19	57.42[c]	31.68 (18.3)	27.35 (31.8)	—	30.81	19.21	18.91	57.51[c]		14.04 (26.9)
$[Pt(dmbn)(R,S,R\text{-}3m\text{-chxn})]^{2+}$	64.34[c]	57.37	31.68 (17.1)	27.40 (33.0)	—	30.91	19.21	18.91	64.19[c]		23.79 (23.2)
$[Pt(NH_3)_2(S,R,R\text{-}4m\text{-chxn})]^{2+}$	58.68	58.34	34.95	27.10 (44.0)	—	30.81	27.35	22.37			
$[Pt(en)(S,R,R\text{-}4m\text{-chxn})]^{2+}$	58.15	57.81	34.95	27.10 (42.8)	—	30.81	27.35	22.37	48.01	47.86	
$[Pt(m\text{-bn})(S,R,R\text{-}4m\text{-chxn})]^{2+}$	58.10	57.81	34.85	27.10 (42.8)	—	30.81	27.30	22.33	57.51	57.27	14.24 13.85 (28.1) (22.0)
$[Pt(dmbn)(S,R,R\text{-}4m\text{-chxn})]^{2+}$	58.10	57.76	34.90	27.10 (41.5)	—	30.81	27.30	22.33	64.39	64.19	23.89 23.69 (26.9)
$[Pt(NH_3)_2(R,S,R\text{-}4m\text{-chxn})]^{2+}$	59.05	58.59 (10)	35.44 (40.3)	26.54 (8.5)	—	31.98	25.59	21.62			
$[Pt(en)(R,S,R\text{-}4m\text{-chxn})]^{2+}$	58.44	58.17	35.39 (38.5)	26.59 (8.5)	—	31.78	25.62	21.40	47.96		
$[Pt(m\text{-bn})(R,S,R\text{-}4m\text{-chxn})]^{2+}$	58.54	58.03	35.46 (39.1)	26.54 (—)[d]	—	32.00	25.59	21.67	57.63	57.32	14.24 13.92 (27.5)
$[Pt(dmbn)(R,S,R\text{-}4m\text{-chxn})]^{2+}$	58.37	58.15	35.41 (37.9)	26.61 (9.8)	—	31.81	25.62	21.42	64.51	64.41	23.89 (25.0)

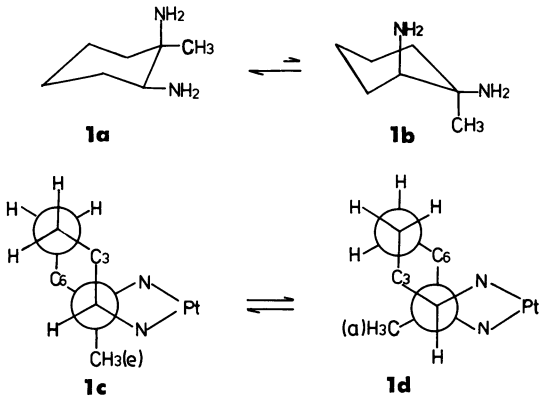
a) Carbon chemical shifts in ppm from external TMS measured vs. internal dioxane. b) Coupling constants (^{195}Pt-C) are found in parentheses in Hz. c) Two chemical shifts due to diamine-ring carbons of m-chxn and another diamine (X) appeared very close to one another. The signal with the stronger intensity was tentatively assigned to X. d) Platinum satellite peaks were observed as shoulders.

prepared from the corresponding methyl derivatives of *cis*-1,2-cyclohexanedicarboxylic acid. 1-Methyl-*r*-1,*c*-2-cyclohexanedicarboxylic acid was synthesized by the Diels-Alder reaction.[7] *t*-3-Methyl-*r*-1,*c*-2-cyclohexanedicarboxylic acid was prepared from the corresponding *c,c*-diastereomer by a literature method.[9] We found that the dicarboxylic aicd **A** obtained from commercially available 4-methyl-1,2-cyclohexanedicarboxylic anhydride was a mixture of *c,c*- and *t,c*-acid by comparing it with an authentic sample prepared according to the literature.[14] It could be separated into two isomers by the method presented in the Experimental section. The attempted optical resolution of 1m-chxn using (2*R*,3*R*)-di-*O*-benzoyltartaric acid was unsuccessful. For other diamines, each optically active enantiomer was prepared.

Conformations of the Chelate Rings. The possible conformations of the free m-chxn ligands and their chelate rings in each complex are shown in **1a—4d**. In the schematic structures of **c** and **d**, each ligand adopts a conformation illustrated in the corresponding structures, **a** and **b**. The symbols of (e) and (a) denote an equatorial and an axial methyl orientation respectively with respect to the cyclohexane ring. Some representative ^{13}C NMR spectra of the Pt^{II} complexes in the δ 10 to δ 40 region are shown in Fig. 1. The chemical shifts and platinum-carbon coupling constants are given in Table 1.

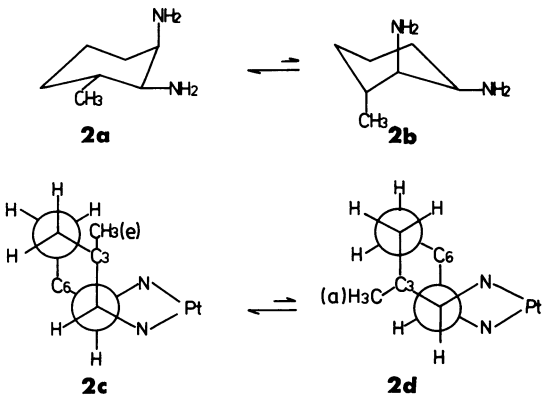
In the ^{13}C NMR spectra of 1m-chxn complexes, three platinum satellites were observed. Of the resonances with the satellite peak due to the skeletal carbons of the cyclohexane ring, one with $^3J_{Pt\text{-}C}$ of 23.2 Hz was assigned to C_6 carbon, applying the β-substituent parameter.[15] The methyl carbon and C_3 carbon, which occupy symmetrical positions about C_1-C_2 bond, showed a 20—22 Hz coupling. For $[Pt(NH_3)_2(m\text{-bn})]^{2+}$ and $[Pt(NH_3)_2(ibn)]^{2+}$ (ibn=2-methyl-1,2-propanediamine), both of which exist in equimolar conformations with a rapid ring inversion, the $^3J_{Pt\text{-}C}$ values have been reported to be 27.3 and 22.4 Hz respectively.[16] The small differences between $^3J_{Pt\text{-}C}$ values due to the three β carbons provide an indication of a roughly equal

probability of λ(**1c**) and δ(**1d**) conformations.



Based on the stereochemistry of the cyclohexane ring, the **1a** conformation, with the larger equatorial methyl and the smaller axial amino group, is more favorable than **1b**. Its conformational behavior prefers the **1c** conformation for the complex. On the other hand, concerning the effects of the substituents on the chelate ring, the **1c** conformation, having a chelate ring with C_3 carbon and the methyl group in axial orientations and C_6 carbon in an equatorial orientation, should be more unfavorable than the **1d** conformation. Because of these competitive steric effects, **1c** and **1d** conformations would seem to be almost equienergetic.

In the ^{13}C NMR spectra of the *R,S,R*-3m-chxn complexes, the signal around 32 ppm was assigned to the C_3 carbon by the aid of the off-resonance proton-decoupling technique. Two $^3J_{Pt-C}$ couplings, of about 18 and 32—33 Hz for C_3 and C_6 carbon respectively, were observed. The absense of additional peaks corresponding to each carbon indicated that the $\lambda \rightleftarrows \delta$ inversion was rapid on the NMR time scale. The



observed $^3J_{Pt-C_3}$ (and $^3J_{Pt-C_6}$) values must be the weighted averages of the **2c** and **2d** conformations, they can be expressed by the following equations:

$$^3J_{Pt-C_3}(\text{obsd}) = p\,{}^3J_{ax(2c)} + (1-p)\,{}^3J_{eq(2d)} \quad (1)$$

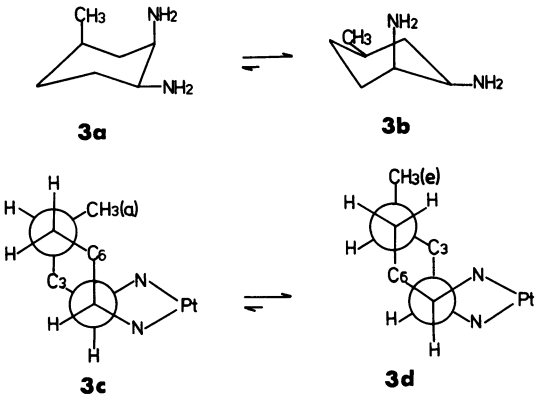
$$^3J_{Pt-C_6}(\text{obsd}) = p\,{}^3J_{eq(2c)} + (1-p)\,{}^3J_{ax(2d)} \quad (2)$$

where p denotes the population of the **2c** conformation and where $^3J_{eq(2c)}$ and $^3J_{ax(2c)}$ are, respectively, the values of $^3J_{Pt-C_6}$ and $^3J_{Pt-C_3}$ when the chelate ring is assumed to have exclusively a rigid conformation, **2c**. Similarly, $^3J_{eq(2d)}$ and $^3J_{ax(2d)}$ are, respectively, $^3J_{Pt-C_3}$ and $^3J_{Pt-C_6}$ when the **2d** conformation is assumed to be fixed. By refering to the literature,[17] $^3J_{eq(2c)}$ was assumed to be equal to $^3J_{eq(2d)}$, and $^3J_{ax(2c)}$ and $^3J_{ax(2d)}$ were assumed to be zero. Then, p is given by Eq. 3:

$$^3J_{Pt-C_6}(\text{obsd}) = p\{{}^3J_{Pt-C_3}(\text{obsd}) + {}^3J_{Pt-C_6}(\text{obsd})\} \quad (3)$$

A calculation from the data in Table 1 yielded p in the range of 0.64—0.67 for the *R,S,R*-3m-chxn complexes. Erickson et al.[17] have reported the p for [Pt(bpy)(pn)]$^{2+}$ (bpy=2,2′-bipyridine) to be 0.72. However, Yano et al.[18] have pointed out that a smaller $^3J_{Pt-C}$ value for an unsymmetrical complex such as a pn complex should be attributed to the puckering effect of the chelate ring rather than to the relative population. Our result showed one of a few cases in which the complex exhibited the intermediate relative population.

In both the **2c** and **2d** conformations of the *R,S,R*-3m-chxn complex, the two β carbons are located in an equatorial and an axial orientation respectively. The axial position in the **2d** conformation is less crowded than that in the **2c** conformation. Therefore the preference for the former conformation was expected. On the contrary, the **2d** conformer would not be preferable on the basis of the stereochemistry of the cyclohexane. The **2c**-conformation preference of about 65% obtained by the use of above NMR results indicated that this conformational equiribrium was influenced more pronouncedly by the stability of the cyclohexane ring than by the steric environment around the chelate ring.



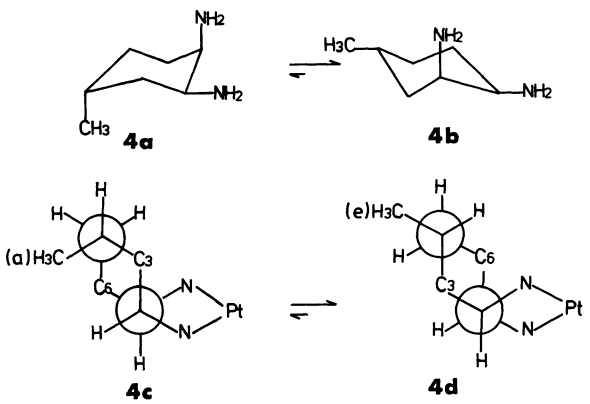
For the *S,R,R*-4m-chxn complexes, there is no large difference between the conformational situations with regard to the chelate rings of **3c** and **3d**, thus, the conformer distribution seems to be exclusively controlled by the stabilities of the cyclohexane ring. The ring inversion between **3a** and **3b** seems improbable because of the 1,3-diaxial interaction. This should lead to a strong preference of one extreme

Table 2. Electronic and CD Spectral Data of $[PtX(m\text{-chxn})]^{2+}$

Complex	Electronic		CD	
	$\nu/10^3\,cm^{-1}$	(log ε)	$\nu/10^3\,cm^{-1}$	($\Delta\varepsilon$)
$[Pt(NH_3)_2(R,S,R\text{-3m-chxn})]^{2+}$	36.0	(1.62)	34.8	(+0.11)
	42 sh	(2.1)	41.2	(−0.07)
	45.0	(2.70)	46 sh	(+0.1)
[Pt(en)(*R,S,R*-3m-chxn)]$^{2+}$	35.4	(1.63)	35.2	(+0.15)
	42 sh	(2.0)	41.5	(−0.07)
	44.6	(2.69)	46 sh	(+0.1)
[Pt(*m*-bn)(*R,S,R*-3m-chxn)]$^{2+}$	35.6	(1.60)	35.3	(+0.12)
	42 sh	(2.1)	41.7	(−0.06)
	44.6	(2.67)	46 sh	(+0.1)
[Pt(dmbn)(*R,S,R*-3m-chxn)]$^{2+}$	35.8	(1.66)	35.6	(+0.17)
	42 sh	(2.2)	41.8	(−0.08)
	44.7	(2.79)	46 sh	(+0.1)
$[Pt(NH_3)_2(S,R,R\text{-4m-chxn})]^{2+}$	35.5	(1.61)	35.2	(−0.16)
	42 sh	(2.2)	41.2	(+0.13)
	45.5	(2.81)	45.0	(−0.26)
[Pt(en)(*S,R,R*-4m-chxn)]$^{2+}$	35.7	(1.63)	35.3	(−0.22)
	42 sh	(2.2)	41.3	(+0.13)
	44.6	(2.71)	46.5	(−0.32)
[Pt(*m*-bn)(*S,R,R*-4m-chxn)]$^{2+}$	35.7	(1.63)	35.6	(−0.26)
	42sh	(2.2)	41.3	(+0.18)
	44.6	(2.73)	46.5	(−0.37)
[Pt(dmbn)(*S,R,R*-4m-chxn)]$^{2+}$	35.8	(1.71)	35.7	(−0.25)
	42 sh	(2.3)	41.5	(+0.16)
	44.8	(2.80)	45.9	(−0.42)
$[Pt(NH_3)_2(R,S,R\text{-4m-chxn})]^{2+}$	35.8	(1.63)	35.0	(−0.15)
	42 sh	(2.3)	41.0	(+0.11)
	45.0	(2.82)	44.8	(−0.27)
[Pt(en)(*R,S,R*-4m-chxn)]$^{2+}$	35.7	(1.63)	35.3	(−0.23)
	42 sh	(2.2)	41.2	(+0.09)
	44.6	(2.70)	45.5	(−0.32)
[Pt(*m*-bn)(*R,S,R*-4m-chxn)]$^{2+}$	35.7	(1.65)	35.3	(−0.25)
	42 sh	(2.3)	41.3	(+0.11)
	44.6	(2.74)	46.5	(−0.33)
[Pt(dmbn)(*R,S,R*-4m-chxn)]$^{2+}$	35.8	(1.65)	35.7	(−0.23)
	42 sh	(2.2)	41.3	(+0.10)
	44.8	(2.79)	46.5	(−0.37)

sh=shoulder.

conformation (**3d**) of the chelate ring. In the ^{13}C NMR spectra of these complexes, the $^3J_{Pt\text{-}C_6}$ coupling of 42—44 Hz and the $^3J_{Pt\text{-}C_3}$ coupling of ≈0 Hz were observed. These facts agree with the above prediction.



In the two conformations (**4c** and **4d**) of the *R,S,R*-4m-chxn complex, the steric effect of the methyl group attached to the γ carbon on the stability of the chelate ring seemed small, as in the *S,R,R*-4m-chxn complex.

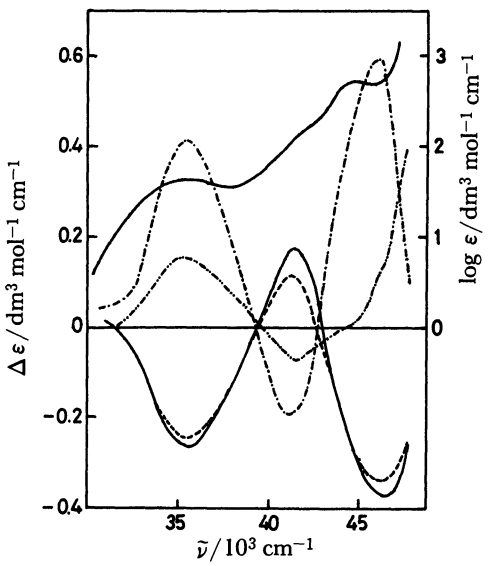


Fig. 2. Electronic and CD spectra of [Pt(en)(*R,S,R*-3m-chxn)]Cl_2 (—·—·—), [Pt(en)(*S,R,R*-3m-chxn)]Cl_2 (—·—·—),[1] [Pt(*m*-bn)(*S,R,R*-4m-chxn)]Cl_2 (——), and [Pt(*m*-bn)(*R,S,R*-4m-chxn)]Cl_2 (——).

Consequently, the conformer population of the chelate ring would seem to depend on the distribution of the two conformations of the free cyclohexane ring. The ^{13}C NMR spectra of the *R,S,R*-4m-chxn complexes indicated the existence of two conformers with a different molar ratio in the equilibrium, as in the case for the *R,S,R*-3m-chxn complexes. By a calculation similar to that used for the latter complexes, the population, *p*, of the **4d** conformation was found to be 0.80—0.83.

The conformational energy barriers for the complexes with a bulky counter ligand(X) might be expected to be higher than those with a smaller one. However, the spectral tendencies of the 1m-, *R,S,R*-3m, and *R,S,R*-4m-chxn complexes suggested that their conformational equilibrium was little affected by the mass of the X.

CD Spectra. The electronic and CD spectra of the complexes are shown in Fig. 2 and Table 2. The *R,S,R*-3m-chxn complexes showed a positive CD band(ca. 35000 cm^{-1}), a negative CD band(ca. 42000 cm^{-1}), and a positive CD band(shoulder ca. 46000 cm^{-1}). The signs and positions of the first two bands of these complexes were almost identical with those of the corresponding bands of the *S,R,R*-3m-chxn complexes[1] (Fig. 2), however, their CD strengths were weaker than those of the latter. Several reports[19-21] have shown that the chiral 1,2-diamine Pt^{II} complexes with a positive CD sign of the ^3E_g transition have a λ conformation. Thus, the λ conformation populated more largely was suggested for the *R,S,R*-3m-chxn complexes. Therefore, the absolute configuration of the present (−)-3m-chxn ligand can be identified as (1*R*,2*S*,3*R*). From the spectral results of both the 4m-chxn complexes, the δ conformations were reasonably deducible. It was concluded that the absolute configurations of the 4m-ligands, whose structures correspond to the *c,c*- and *t,c*-configurations, were (1*S*,2*R*,4*R*) and (1*R*,2*S*,4*R*) respectively.

Hawkins et al.[21] have reported the estimated value of the conformer population of $[Pt(NH_3)_2((S)$-3,3-dmbn$)]^{2+}$ (3,3-dmbn=3,3-dimethyl-1,2-butanediamine) from a comparison of the CD intensities of the ^1E_g band. Comparing the CD intensities of the present *R,S,R*-3m-chxn complexes with those of the *S,R,R*-3m-chxn complexes,[1] the intensity ratios were found to be 0.37 (the band around 35000 cm^{-1}) and 0.34 (the band around 41000 cm^{-1}) for $[Pt(NH_3)_2L]^{2+}$, and 0.37 (the band around 35000 cm^{-1}) and 0.35 (the band around 42000 cm^{-1}) for $[Pt(en)L]^{2+}$. If the contribution of the chiral atoms to the Cotton effect of the above bands is negligibly small, and if the $\Delta\varepsilon$ value of the *R,S,R*-3m-chxn complex, which presumably has an extremely fixed conformation, is nearly equal to that of the *S,R,R*-3m-chxn complex, the more favorable λ conformer populations of the *R,S,R*-3m-chxn complexes can be calculated to range from 0.65 to 0.68. These values were in excellent agreement with those estimated by means of NMR analyses. However, for the *R,S,R*-4m-chxn complexes the δ conformer population derived from a similar calculation did not agree with those obtained by NMR analyses. There remain some questions in these CD analyses, one of them being the lack of a common CD intensity value for the complexes with a fixed conformation.

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