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The Preparations, Properties and Structures of *trans*-$[Rh(CN)_2(tn)_2]^+$

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The title dicyano-complex of Rh(III) was newly synthesized. Stepwise ligand substitutions in an aqueous medium through *trans*-$[RhCl_2(tn)_2]^+$, *trans*-$[Rh(SO_3)_2(tn)_2]^-$, *trans*-$[Rh(CN)(SO_3)(tn)_2]$, and *trans*-$[Rh(CN)Cl(tn)_2]^-$ were studied. The final substitution of Cl^- of *trans*-$[Rh(CN)Cl(tn)_2]^-$ by CN^- was effected in a mixed medium of DMSO, ethanol, and H_2O (8 : 1 : 1). The ligand field tetragonal parameters of D_t ca. −380 cm^{-1} were estimated based on the lower d–d absorption maximum at 36100 cm^{-1}. The sharp IR peaks of ν (C≡N) were observed at 2115 cm^{-1} (nitrate) and 2116, 2131 cm^{-1} (perchlorate). The slight splitting detected for solid compound of the perchlorate was attributed to the presence of a structurally different complex species with respect to the Rh–C≡N bondings in the crystal. The X-ray crystal data are: *trans*-$[Rh(CN)_2(tn)_2](NO_3)$: monoclinic, space group $P2_1/n$, $a=11.626(4)$, $b=6.3624(6)$, $c=10.026(3)$ Å, $\beta=113.54(4)°$, $D_m=1.78$, $D_c=1.784$ g cm^{-3}, $Z=2$; *trans*-$[Rh(CN)_2(tn)_2](ClO_4)$: triclinic, space group $P\bar{1}$, $a=9.230(5)$, $b=12.690(3)$, $c=6.861(2)$ Å, $\alpha=101.36(3)°$, $\beta=106.10(3)°$, $\gamma=76.42(3)°$, $D_m=1.80$, $D_c=1.800$ g cm^{-3}, $Z=2$. In these two crystal lattices, the *trans*-$[Rh(CN)_2(tn)_2]^+$ cations occupy the special positions of the inversion center, and the Rh-tn six-membered chelate rings appear in the chair form. While all of the bond distances and angles were well conserved, an appreciable variation appeared in the dihedral angles defined in the chair chelate rings (N–Rh–N : N–C···N–C and N–C···N–C : C–C–C). This structural variation in the Rh-tn chelate rings is responsible for the complicated splittings of the IR bands of the perchlorate, especially, in the CH_2 rocking region of 880—970 cm^{-1}. Other important geometrical data of the complex are (in mean values): Rh–N=2.09, Rh–C=2.03 Å, N–Rh–N (in chelate ring)=91.8°

We recently reported the syntheses, properties and structures of the cyano-ammine complexes of Rh(III), *trans*-$[Rh(CN)_2(NH_3)_4]^+$ and *trans*-$[Rh(CN)_2(en)_2]^+$.[1)] The work has been extended to a corresponding complex containing 1,3-propanediamine (abbreviated by tn) ligands, *trans*-$[Rh(CN)_2(tn)_2]^+$, in the present study. Although the synthetic reactions involved are essentially similar to those employed in the previous work concerning the NH_3 and en complexes, very mild reaction conditions and careful isolations of the compounds are necessary in the present case. While many X-ray crystal structure analyses concerning the tn chelate complexes have revealed mostly the chair form of rings, some instances appeared in which the M-tn chelate ring appeared in the skewboat form.[2—4)] Particularly, we characterized the conformational alteration (chair↔skewboat) of one of the chelate rings of *trans*-$[Co(CN)_2(tn)_2]^+$ in different phases of the chloride crystal.[5)] Emphasis was focused on the special sensitivity of the IR absorption pattern in the CH_2 rocking region (870—970 cm^{-1}) upon these structural alterations.

In order to establish a detailed understanding of the relation between the IR spectroscopic properties and the structure of the $[MX_2(tn)_2]^{n+}$ complexes, the present complex was analyzed by X-ray regarding the three kinds of crystal lattices. On the basis of normal coordinate analyses, the IR absorption pattern observed for the solid compounds could be characterized in relation to the detailed structural variation of the six-membered chelate rings in the chair form.

Experimental

Preparation. ***trans*-$[RhCl_2(tn)_2](ClO_4)$.** The reported method for the preparation of the nitrate[6)] was revised. In the present method, in which double amounts of 1,3-propanediamine and an extremely longer reaction time (about 8 h) was employed, and lastly perchloric acid instead of nitric acid was used for isolation of the complex, gave a yield of up to ca. 80% (50% in the literature). The perchlorate could be easily converted to the chloride through an anion-exchange resin.

***trans*-$[Rh(CN)(SO_3)(tn)_2]\cdot H_2O$.** To a solution of 0.92 g of *trans*-$[RhCl_2(tn)_2]Cl$ in 40 ml H_2O, 4.00 g of Na_2SO_3 was added. The solution was heated to 90 °C for 2 h. During the first ten minutes of this reaction, the characteristic yellow color of the starting material was lost. The white precipitate was separated and collected on a filter and washed by ethanol and air dried. This was adsorbed on a column of anion exchange resin (MCI GEL CA08P 75—150 µm in Cl^- form) and eluated with 0.5 M LiCl (1 M=1 mol dm^{-3}). After condensed the solution, white powder was obtained. The ultra-violet absorption spectrum[1)] suggested this compound to be *trans*-$Na[Rh(SO_3)_2(tn)_2]$. Yield: 0.85 g (72%). To an aqueous solution (40 ml) containing 0.4 g of the above intermediate (*trans*-$Na[Rh(SO_3)_2(tn)_2]$), 2 g of NaCN was added. The mixture was left standing for 2 d at 25 °C under constant agitation. The resultant solution was passed through a column of anion-exchange resin (MCI GEL CA08P 75—150 µm in Cl^- form), followed by a column of cation-exchange resin (Dowex 50W-X8 in Li^+ form). Complete evaporation of the eluent left a white powder, which was thoroughly washed by ethanol to remove LiCl, and air-dried. Yield: 0.18 g (55%).

Analytical: Found: C, 22.26; H, 5.78; N, 18.05. Calcd for *trans*-$[Rh(CN)(SO_3)(tn)_2]\cdot H_2O$: C, 22.41; H, 5.91; N, 18.66%.

***trans*-[Rh(CN)Cl(tn)$_2$](ClO$_4$).** A half gram of *trans*-[Rh(CN)(SO$_3$)(tn)$_2$] was treated with 5 ml concd HCl at 60 °C. Within 5 min, the SO$_2$ gas evolution ceased. To the resultant transparent solution a small portion (ca. 0.5 ml) of perchloric acid (70%) was added. Ethanol was then added by ice cooling (caution for explosion !) to give a white fine crystalline powder, which was filtered and washed with ethanol and air-dried. Yield: 0.34 g (59%). Since this compound was hygroscopic, the analytical results did not coincide with the calculated values. However, carefully measured IR and UV absorption spectra suggested that a ligand substitution of SO_3^{2-} to Cl^- was sufficiently effected in the concd HCl solution, similarly to the corresponding reactions for the NH$_3$ and en complexes.[1]

***trans*-[Rh(CN)$_2$(tn)$_2$]Cl·1/2H$_2$O.** One and half grams of *trans*-[Rh(CN)Cl(tn)$_2$](ClO$_4$) and NaCN in a 10 ml mixed medium of DMSO–EtOH–H$_2$O (8 : 1 : 1) were vigorously stirred at 80 °C for 30 min. The mixed medium was then evaporated at 40 °C to near dryness. After ethanol was added, the white solid was filtered and washed with ethanol and air-dried. This was adsorbed on a column of a cation exchange resin (Dowex 50W-X8 in Li$^+$ form). Elution with a 0.2 M LiCl solution enabled the collection of the desired portion while monitoring with the ultraviolet absorption spectra. After concentration at 40 °C, the white solid was precipitated by the addition of ethanol, which was filtered: the ethanol washed and air dried. Yield: 0.75 g (61%). Analytical: Found : C, 27.46; H, 6.28; N, 24.05%. Calcd for *trans*-[Rh(CN)$_2$(tn)$_2$]Cl·1/2H$_2$O : C, 27.63; H, 6.10; N, 24.18%.

***trans*-[Rh(CN)$_2$(tn)$_2$](NO$_3$) and *trans*-[Rh(CN)$_2$(tn)$_2$](ClO$_4$).** The transformations from the chloride hemihydrate to the nitrate and perchlorate were easily accomplished by the addition of concd nitric acid and concd perchloric acid, respectively, to a concentrated aqueous solution of the chloride hemihydrate. The produced crystals during ice cooling were filtered and washed with ethanol. The yields were quantitative.

Analytical: Found : C, 26.39; H, 5.28; N, 26.41%. Calcd for *trans*-[Rh(CN)$_2$(tn)$_2$](NO$_3$) : C, 26.31; H, 5.52; N, 26.85%.

Analytical: Found : C, 23.55; H, 4.72; N, 20.08%. Calcd for *trans*-[Rh(CN)$_2$(tn)$_2$](ClO$_4$) : C, 23.86; H, 5.01; N, 20.87%.

N-deuteriated compounds could be obtained after three times of recrystallization from the D$_2$O solution while monitoring the IR spectra, respectively.

Spectroscopic Measurements. IR and Raman spectra were obtained using a Perkin–Elmer 1600 FTIR spectrometer (4000—650 cm^{-1}) and a Hitachi IR-F spectrometer (700—200 cm^{-1}), as well as a Jobin-Ybone Ramanor 1000 spectrometer with Ar$^+$-ion laser (NEC GLG 3300) 5145 Å excitation. The Raman spectrometer was also used for luminescence spectroscopy with the adaptation of a high-pressure mercury lamp; an appropriate filter system was used as an excitation source (312 nm line). Visible-ultraviolet absorption spectra were recorded on a Hitachi U-3400 spectrometer. Proton and ^{13}C NMR measurements were carried out using a JEOL GSX-400 spectrometer. One tenth of a gram of *trans*-[Rh(CN)$_2$(tn)$_2$]Cl was dissolved in 1 ml D$_2$O containing one drop of concd DCl (D$_2$O). TSP-d_4 was used as an external standard.

Normal Coordinate Analysis. A normal coordinate analysis was performed by Wilson's GF method using library programs (BGLZ and LSMB)[7] of the Computer Center of the University of Tokyo, which were transferred to a personal computer (NEC PC-9801VM2); the input–output control procedures were revised.

X-Ray Crystal Structure Analyses. Single-crystal X-ray measurements were performed on a Rigaku AFC-5 four-circle automated diffractometer. The details concerning the experimental conditions as well as crystal data are collected in Table 1. An absorption correction of North et al.[8] was applied. Most of the computational work was carried out using a HITAC 682H computer at the Computer Center of the University of Tokyo, using a library program system for X-ray crystallography, (UNICS III[9]).

***trans*-[Rh(CN)$_2$(tn)$_2$](NO$_3$).** The complex cations are located on one of the special positions of the inversion symmetry ($P2_1/n$, $Z=2$). The nitrate anion must also be placed on the other special position of the inversion symmetry. However, because of the trigonal planner geometry of the nitrate anion, this is impossible, unless some disorder structure is assumed in this crystal (vide infra). The initial positions of the C and N atoms of the cyanide ion and the coordinating N atoms were determined by a Patterson synthesis. Following, successive refinements by Fourier procedures yielded all of the non-hydrogen atom positions of the complex cation. The difference Fourier map exhibited electron density peaks at (x=ca.−0.1, y=ca. 0.4, z=ca. 0.4) and (x=ca. 0.1, y=ca. 0.4, z=ca. 0.4) and a vague peak at around (x=0, y=1/2, z=1/2). A least-squares procedure assigning the former two to the oxygen atoms and latter to the nitrogen atom of NO_3^- with a half multiplicity gave an R value of 0.08. At this stage, all of the hydrogen atoms were identified on the difference Fourier map. After five cycles of a block-diagonal least-square treatment with anisotropic temperature factors, the R value was reduced to 0.0363. The resultant position of the nitrogen of NO_3^- was moved somewhat towards the midpoint of the two oxygen atoms, and the anisotropic temperature factors of the nitrogen atom was very large; the position of the remaining oxygen atom of the NO_3^- could not be clearly determined. The special position (x=0, y=1/2, z=1/2: inversion center) must be located at an intermediate position between the nitrogen and the other oxygen atoms of NO_3^-. The separation of the electron density of the nitrogen and other oxygen atoms of the two NO_3^- anions with a half multiplicity, which are connected by inversion symmetry, could not be completed in the least-squares treatments. Since the analyzed structure of the complex cation was quite reasonable, even at this stage, the numerical results are collected in Tables 2 and 3.

The tables of the observed and calculated structure factors, anisotropic temperature factors and coordinates of hydrogen atoms resulting from the present study are deposited as Document No. 66024 at the Office of the Editor of Bull. Chem. Soc. Jpn.

***trans*-[Rh(CN)$_2$(tn)$_2$](ClO$_4$).** The two non-equivalent complex species are located at the special positions with an inversion symmetry in the unit cell ($P\bar{1}$, $Z=2$). The initial phases determined by the Rh and ClO_4^-, whose positions were obtained on the Patterson synthesis, yielded the atomic positions of all of the non-hydrogen atoms on a Fourier map. After several cycles of block-diagonal least-squares refine-

Table 1. Summary of X-Ray Data Collections, Crystal Data, and Structure Refinements

	trans-$[Rh(CN)_2(tn)_2](NO_3)$	*trans*-$[Rh(CN)_2(tn)_2](ClO_4)$	*trans*-$[Rh(CN)_2(tn)_2]Cl \cdot 1/2H_2O$
Formula	$RhC_8N_7O_3H_{20}$	$RhC_8N_6O_4H_{20}Cl$	$RhC_8N_6O_{0.5}H_{21}Cl$
Formula weight	365.198	402.643	347.645
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$
a/Å	11.626(4)	9.230(5)	12.874(4)
b/Å	6.3624(6)	12.690(3)	13.810(3)
c/Å	10.026(3)	6.861(2)	9.272(3)
α/deg		101.36(3)	91.62(2)
β/deg	113.54(4)	106.10(3)	108.45(2)
γ/deg		76.42(3)	114.06(2)
V/Å^3	679.9(4)	743.1(5)	1404.1(7)
Z	2	2	4
D_c/cm^{-3}	1.784	1.800	1.644
D_m/cm^{-3}	1.79	1.80	1.68
Crystal size/mm	$0.47 \times 0.35 \times 0.05$	$0.38 \times 0.50 \times 0.37$	$0.30 \times 0.18 \times 0.12$
Scan mode (ω–2θ)	$2 \leqq 2\theta < 55$	$2 \leqq 2\theta < 55$	$2 \leqq 2\theta < 55$
Scan width/deg	$1.10 + 0.45\tan\theta$	$1.10 + 0.45\tan\theta$	$1.20 + 0.45\tan\theta$
Scan speed/deg min^{-1}	4.0	4.0	4.0
No. of refl. measd.	2255	3695	7664
No. of unique refl. with $F_o > 3\sigma(F_o)$	1676	3065	4607
R	0.0363	0.0264	0.109

ments, all of the hydrogen atoms could be identified based on the difference Fourier synthesis. The final block-diagonal treatments, which applied anisotropic temperature factors for the non-hydrogen atoms, gave an R value of 0.0264. The resultant atomic parameters and some important geometrical values are collected in Tables 2 and 3.

***trans*-$[Rh(CN)_2(tn)_2]Cl \cdot 1/2H_2O$.** We also analysed the chloride crystal. The structure was solved by an ordinary heavy-atom method. However, almost all of the hydrogen atoms were not clearly found on the difference Fourier map, and introducing all of the hydrogen atoms to the ideal positions did not improve the R value appreciably (R=0.109 without hydrogen atoms in the $P\bar{1}$ space). In the chloride unit cell, since the four non-equivalent complex cations having two chair rings are located at the special positions with inversion symmetry, all of the complex cations have the C_{2h} point symmetry. It was found that the dihedral angles involved in the complex cations vary over a range of 144—155° in α and 113—119° in β, although the bond distances and angles are in the range of ordinary values.

Results and Discussion

The present complex, *trans*-$[Rh(CN)_2(tn)_2]^+$, was synthesized through a synthetic reaction route that is essentially similar to those employed for the corresponding NH_3 and en complexes.[1)] However, the intermediates involved in the present work, such as *trans*-$[Rh(CN)(SO_3)(tn)_2]$ and *trans*-$[Rh(CN)Cl(tn)_2]^+$, are quite soluble and, sometimes, unstable in an aqueous solution, compared to the corresponding complexes of NH_3 and en. The intermediate cyanosulphito complex, *trans*-$[Rh(CN)(SO_3)(tn)_2]$, was first obtained through the bis(sulphito) complex, *trans*-$[Rh(SO_3)_2(tn)_2]^-$, while direct syntheses from the dichloro complexes were possible in the NH_3 and en cases. Isolation of the present cyano-chloro intermediate was effected by a careful addition of sufficient amounts of ethanol after a very long-time (2 d) room-temperature reaction; while very smooth reactions at higher temperatures, however, took place in the cases of the NH_3 and en complexes. Ligand substitution of Cl^- by CN^- in the last reaction took place in a newly arranged mixed medium (DMSO : EtOH : H_2O=8 : 1 : 1).

The UV spectra are presented in Fig. 1. The lower frequency band at 31600 cm^{-1} is assignable to the ligand field transition of the $^1E_g^a$ $(D_{4h}) \leftarrow {}^1A_{1g}$ and the higher band at 41400 cm^{-1} to the $^1E_g^b$ $(D_{4h}) \leftarrow {}^1A_{1g}$. Similar to the cases of the NH_3 and en complexes, no band splitting appeared due to the $^1A_{2g}$ $(D_{4h}) \leftarrow {}^1A_{1g}$ and the $^1B_{1g} \leftarrow {}^1A_{1g}$ transitions. The tetragonal parameters (D_t) can be estimated to be ca. −880 cm^{-1}, by assuming[10)] that the $^1A_{2g} \leftarrow {}^1A_{1g}$ band is located at the same position as the $^1T_{1g} \leftarrow {}^1A_{1g}$ band of $[Rh(NH_3)_6]^{3+}$.

Similar to the NH_3 and en complexes,[1)] the present complex compounds also exhibit luminescence upon ultraviolet irradiation at low temperatures (ca. 78 K). The band maxima, located at 18300 cm^{-1} (chloride), 18300 cm^{-1} (perchrorate), and 19000 cm^{-1} (nitrate), were recorded for the d_4-tn complex compounds. This luminescence must be due to an electronic transition from the spin–orbit component(s) of the lowest ligand-field state of $^3T_{1g}(O_h)$. A similar luminescence was observed for $[Rh(NH_3)_6]^{3+}$ and other Rh(III) complexes.[11)]

Proton NMR signals appeared at 1.77, 2.87, and 4.40

Table 2. Positional Parameters ($\times 10^4$) *trans*-$[Rh(CN)_2(tn)_2](NO_3)$, *trans*-$[Rh(CN)_2(tn)_2](ClO_4)$

Atom	x/a	y/b	z/c	$B_{eq}/Å^2$ b)	Atom	x/a	y/b	z/c	$B_{eq}/Å^2$
			trans-$[Rh(CN)_2(tn)_2](NO_3)$						
Rh	0	0	0	1.2					
C	−1075(6)	2579(11)	−833(7)	1.8					
N	−1697(6)	4006(10)	−1328(7)	2.6					
N1	1593(5)	1609(9)	61(6)	1.8					
N2	−442(5)	−1111(9)	−2115(6)	1.9					
C1	1551(7)	2554(12)	−1308(8)	2.3					
C2	−159(7)	306(13)	−3139(7)	2.4					
C3	1206(7)	969(13)	−2537(8)	2.6					
N(O)	0(0)	5000(0)	5000(0)	7.7					
O1	−82(2)	529(4)	559(2)	2.8					
O2	−75(2)	391(4)	389(3)	3.0					
O3	70(3)	428(6)	601(4)	6.5					
			trans-$[Rh(CN)_2(tn)_2](ClO_4)$						
Rh(1)	0	0	0	1.45	Rh(2)	0	5000	0	1.45
C(1)	230(5)	1189(3)	−1426(6)	2.04	C(2)	−670(5)	4153(3)	1714(6)	2.10
N(1)	261(5)	1858(3)	−2267(7)	3.10	N(2)	−1056(6)	3688(4)	2682(7)	3.38
N1(1)	−450(4)	1183(3)	2473(5)	2.22	N1(2)	1159(4)	5823(3)	2714(5)	2.16
N2(1)	−2318(4)	254(3)	−1551(6)	2.38	N2(2)	1971(4)	3785(3)	−42(6)	2.19
C1(1)	−1904(6)	1251(4)	3071(7)	3.02	C1(2)	2774(6)	5900(4)	2888(7)	2.81
C2(1)	−3476(5)	455(4)	−324(8)	3.08	C2(2)	3470(5)	4146(4)	471(8)	2.87
C3(1)	−3301(6)	1448(5)	1301(9)	3.58	C3(2)	3816(6)	4787(4)	2606(8)	3.23
					Cl	3632(2)	2145(1)	−4880(2)	3.26
					O1	3212(5)	2041(3)	−7082(5)	4.19
					O2	3145(6)	1281(5)	−4279(7)	5.77
					O3	2866(8)	3185(5)	−4085(8)	8.28
					O4	5248(6)	2030(5)	−4169(9)	7.36

a) Hydrogen atoms are omitted. b) Isotropic equivalent thermal parameters is given as $B_{eq}=4/3(\sum_i \sum_j B_{ij}a_i a_j)$.

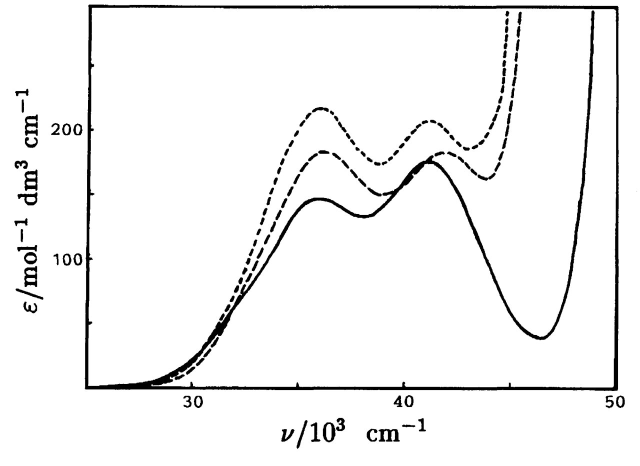

Fig. 1. Electronic absorption spectra of *trans*-dicyano ammine complexes of Rh(III). (a) — *trans*-$[Rh(CN)_2(NH_3)_4]Cl\cdot H_2O$, (b) --- *trans*-$[Rh(CN)_2(en)_2]Cl$, (c) ···· *trans*-$[Rh(CN)_2(tn)_2](ClO_4)$.

ppm (intensity ratio of the former two was estimated to be 1.00 : 2.02). These were assigned to the top CH_2, side CH_2, and NH_2 protons, respectively. The ^{13}C NMR showed three signals at 30.1, 45.6, and 140 (doublet) ppm. The former two were assigned to the ring carbons of N-$\underline{C}$-C and C-$\underline{C}$-C, respectively. The highest doublet was assigned to the cyanide carbons. The observed splitting of the cyanide carbon signal was attributed to the nuclear-nuclear interaction of ^{113}Rh and ^{13}C. The coupling constant was estimated to be $J_{Rh-C}=39$ Hz. These proton and ^{13}C NMR data are consistent with the *trans*-dicyanobis(1,3-propanediamine) geometry of the complex.

The clear correlation of the IR absorption spectra in the 870—970 cm^{-1} region to the conformation of the M-tn chelate ring was studied.[5] That is, a solid sample of *trans*-$[Co(CN)_2(tn)_2]Cl\cdot H_2O$, in which one of the Co-tn rings in the complex is in a skewboat conformation, while another is in a chair form, exhibits three distinct peaks in this region; however, in the spectra of *trans*-$[Co(CN)_2(tn)_2]Cl\cdot 3H_2O$,[5] and *trans*-$[Co(NO_3)_2(tn)_2](NO_3)$,[12] in which both Co-tn rings have been confirmed by X-ray to be chair form, two clear peaks are observed. Normal coordinate analyses of these two conformational structures revealed that the vibrational modes appearing in this frequency region comprise mainly CH_2 (side) and CH_2 (top) rocking displacements within the ring; they are thus quite sensitive to the conformational structure of the ring. The IR spectra of the present *trans*-$[Rh(CN)_2(tn)_2]^+$ cation in the three different crystal lattices are presented in Fig. 2. Since the nitrate shows two clear peaks at 900.2 cm^{-1} and

Table 3. Intra-Molecular Geometrical Parameters of *trans*-$[Rh(CN)_2(tn)_2]^+$ Complex. (Bond Distance/Å, Bond Angle/deg, and Dihedral Angle/deg)

	Nitrate	Perchlorate	
		(1)	(2)
Rh–C	2.030(5)	2.029(5)	2.034(5)
C–N	1.140(7)	1.129(7)	1.138(8)
Rh–N1	2.096(5)	2.098(4)	2.087(3)
Rh–N2	2.093(4)	2.089(3)	2.093(3)
N1–C1	1.484(8)	1.491(7)	1.487(7)
N2–C2	1.500(8)	1.481(7)	1.487(7)
C1–C3	1.514(8)	1.515(7)	1.521(6)
C2–C3	1.517(8)	1.513(7)	1.518(7)
Rh–C–N	178.4(4)	175.7(4)	179.2(4)
N1–Rh–N2	93.0(2)	91.7(1)	90.2(1)
N1–Rh–C	90.5(2)	89.8(2)	88.6(2)
N2–Rh–C	89.7(2)	87.4(2)	89.8(2)
Rh–N1–C1	117.9(3)	117.1(3)	117.7(3)
Rh–N2–C2	117.3(3)	117.9(3)	117.5(3)
N1–C1–C3	112.4(5)	112.0(5)	113.1(4)
N2–C2–C3	112.0(4)	111.2(5)	112.1(4)
C1–C3–C2	113.9(6)	113.5(4)	115.1(4)
(Rh,N1,N2): (N1,N2,C1,C2)	149.5(3)	146.7(2)	143.0(2)
(N1,N2,C1,C2): (C1,C2,C3)	116.4(8)	115.3(5)	120.7(5)

948.3 cm^{-1}, the complex cation must have two chair-form rings in C_{2h} point symmetry, while the other two compounds exhibit very complicated split patterns for the bands. These spectra could not be easily characterized within the known categories of IR pattern for this type of complex. In addition, the ν (C≡N) bands of the perchlorate and chloride appears to be slightly split by 15 cm^{-1} (2136, 2150 cm^{-1}) and 4 cm^{-1} (2136, 2140 cm^{-1}), respectively, while no splitting was observed for the nitrate (2140 cm^{-1}). The splittings were correspondingly detected in the Raman spectra: 15 cm^{-1} for the perchrolate (2116, 2131 cm^{-1}), 4 cm^{-1} for the chloride (2117, 2121 cm^{-1}), and no splitting for the nitrate (2115 cm^{-1}). Konya et al.[12] have noted that the splitting of the ν (C≡N) band for the dicyano complexes indicates the *cis*-geometry. This argues strongly against the present cases; since all other spectroscopic data indicated the *trans*-geometry. We intend to further study the details concerning the correlation between the IR (and Raman) spectroscopic behavior and the structure of the *trans*-dicyano complexes having the simplest six-membered chelate ring comprising 1,3-propanediamine. Along this line of research, we performed X-ray crystal structure analyses of the present complex compounds.

As already described in the Experimental Section, in the nitrate crystal, the two complex cations involved in the $P2_1/c$ unit cell are equivalent, and are located at the special positions of the inversion symmetry. The perchlorate cell of the $P\bar{1}$ space group contains two non-equivalent complex species, both of which are located at the special positions of the inversion symmetry. An important feature to be noted is that all of the complex cations analyzed in the nitrate and perchlorate lattices appeared in the two-chair conformational structure and having an effective point symmetry of C_{2h} (Fig. 3). The situation is the same in the chloride lattice (see Experimental Section).

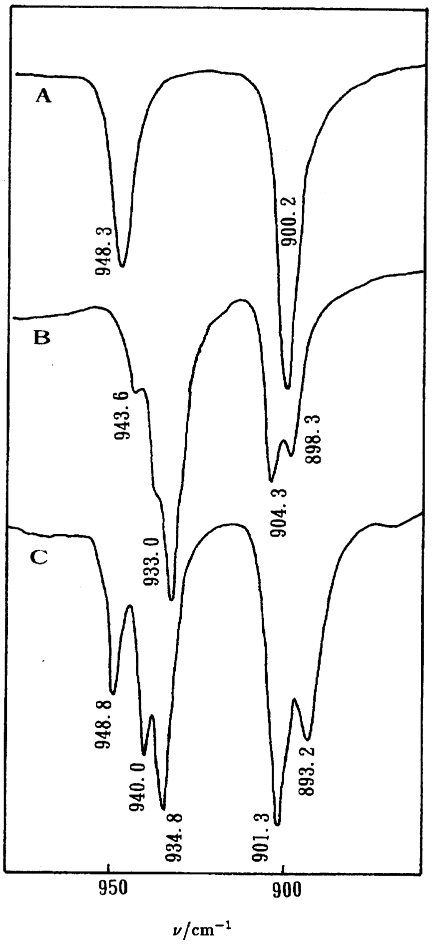

Fig. 2. Infrared absorption spectra of *trans*-$[Rh(CN)_2(tn)_2]^+$ complex in three different crystals. (A) *trans*-$[Rh(CN)_2(tn)_2](NO_3)$, (B) *trans*-$[Rh(CN)_2(tn)_2](ClO_4)$, and (C) *trans*-$[Rh(CN)_2(tn)_2]Cl\cdot 1/2H_2O$.

An examination of the X-ray results yielded a reasonable interpretation of the IR and Raman splitting of the ν (C≡N) bands observed for the perchlorate. That is, one of the two non-equivalent complexes in the perchlorate lattice has a Rh–C≡N bond which deviates as much as ca. 4° from linearity, presumably due to crystal packing forces; the other, as well as that in the nitrate

Table 4. Observed[a)] and Calculated[b)] Vibrational Frequencies (ν/cm^{-1}) of *trans*-$[Rh(CN)_2(tn)_2]^+$ in the CH_2 Rocking Region

Nitrate		Perchlorate				Assignment[c)]
		(1)		(2)		
Obsd	Calcd	Obsd	Calcd	Obsd	Calcd	
948.3	ν_{61}:956	943.6	ν_{61}:975	933.0	ν_{61}:964	Side CH_2
	ν_{62}:957		ν_{62}:975		ν_{62}:963	Side CH_2
938.0(R)	ν_{63}:925		ν_{63}:945		ν_{63}:937	Side CH_2, Top CH_2
	ν_{64}:923		ν_{64}:944		ν_{64}:935	Side CH_2, Top CH_2
900.2	ν_{65}:910	904.3	ν_{65}:915	898.3	ν_{65}:908	Top CH_2
	ν_{66}:906		ν_{66}:909		ν_{66}:901	Top CH_2

a) (R): Raman effect, others are IR bands. b) Based on the X-ray analyzed geometries in the two different crystal lattices (see text). force constants [K,H, F (mdyne/Å]; K(Rh–N) = 1.543, K(Rh–C) = 1.80, K(N–C) = 5.60, K(C–C) = 5.80, K(C–H) = 4.00, K(N–H) = 4.80, K(C≡N) = 16.47, H(N–Rh–N) = 0.36, F(N–Rh–N) = 0.15, H(Rh–N–C) = 0.35, F(Rh–N–C) = 0.15, H(Rh–C≡N) = 0.30, F(Rh–C≡N) = 0.15, H(N–C–C) = 0.35, F(N–C–C) = 0.15, H(C–C–C) = 0.35, F(C–C–C) = 0.15, H(C–Rh–N) = 0.30, F(C–Rh–N) = 0.15, H(Rh–N–H) = 0.25, F(Rh–N–H) = 0.25, H(C–N–H) = 0.30, F(C–N–H) = 0.40, H(H–N–H) = 0.40, F(H–N–H) = 0.20, H(N–C–H) = 0.32, F(N–C–H) = 0.45, H(C–C–H) = 0.32, F(C–C–H) = 0.45, H(H–C–H) = 0.40, F(H–C–H) = 0.30, π(RhN4) = 0.25 (mdyne·Å). c) Assignments were made based on the PED valus of the modes.

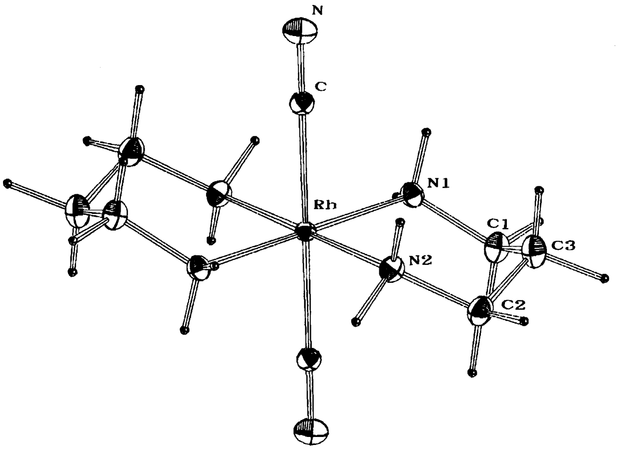

Fig. 3. ORTEP drawing of the structure of *trans*-$[Rh(CN)_2(tn)_2]^+$ in a nitrate crystal.

lattice, have almost normal linear Rh–C≡N bondings (see Table 3). The presence of complex cations having appreciably different Rh–C≡N bond geometries (angles) in the lattice could be the reason for the splitting of the IR and Raman bands of ν (C≡N). In other words, the present study has given evidence for a limited significance of the IR splitting rule on the ν (C≡N) band for the determination of the *cis*-geometry of the dicyano-type complex.

It must firstly be noticed that the bond distances and angles are well conserved in all of the complex cations analysed. However, a remarkable variation in the dihedral angles of N–Rh–N : N-C···N-C (α) and N-C···N-C : C–C–C (β) definable in the chair form ring should be noticed. That is, they vary over the range of 143°—149° for α and 115°—121° for β (Table 3). In general, those rings having a smaller α appear to have a larger β, and vice versa.

We performed normal coordinate analyses of the *trans*-$[Rh(CN)_2(tn)_2]^+$ moiety in order to elucidate the IR spectroscopic properties, especially in 800—950 cm^{-1} region. The G matrices were constructed based upon the X-ray analysed geometries with a precise C_i point symmetry. In the present analyses, the hydrogen atoms assumed to be in the standard positions (N–H: 1.02 Å, ∠H-N-H: 104.5°, C–H: 1.10 Å, ∠H-C-H: 109.4°) were used, rather than those from the X-ray results. Almost all of the force constant values (Urey–Bladley type) were transferred from a previous paper concerning the corresponding complex of Co(III). They were optimized, including the presently introduced values of K (Rh–N): 1.40 and K (Rh–C): 1.80 (mdyne/Å) (see footnote of Table 4). Although modes sensitive to the ring structure were also found in the 1150—1270 cm^{-1} (C–N stretching and C–C stretching) and 740—810 cm^{-1} (NH_2 rocking) regions, the characteristic sensitivity should be mentioned again concerning the six normal vibrations appeared in the 880—980 cm^{-1} regions, which are CH_2 rocking vibrations coupled to some extent with the N-C, C-C stretching and NH_2 rocking motions in the rings. Table 4 shows the calculated normal-mode frequencies in this region. The included assignments were assisted by the Raman spectroscopy, in which an evident scattering line was detected at 938 cm^{-1} for the nitrate. It was found that the frequencies apparently depend on the dihedral angles (α and β). That is, frequency differences as large as ca. 8 and ca. 13 cm^{-1} were calculated for the two modes (ν_{60} or ν_{61} and ν_{63} or ν_{64}), respectively, based on the two geometries of the complex found in the perchlorate lattice. These amounts of frequency difference can be compared with the observed IR splittings (11 cm^{-1}

and 15 cm^{-1}) for the ca. 870 and ca. 970 cm^{-1} bands. In other words, the present normal coordinate analysis implies that a slight variation in the dihedral angles of the tn chelate rings could cause frequency changes in the $\mathrm{CH_2}$ rocking modes corresponding to the observed splittings in the IR spectrum of the perchlorate.

In the chloride lattice, the four non-equivalent complex cations having two chair rings are located at the special positions having an inversion symmetry (C_{2h} symmetry); the dihedral angles of the complexes were estimated to vary over the range 144—155° (α) and 113—119° (β), although the structure refinement was not sufficiently completed (see Experimental Section). The IR spectrum feature of the chloride is in line with the present discussions (Fig. 2).

Based on the results of a previous study concerning the Co(III) complex, the IR spectra of the *trans*-di(acido)bis(1,3-propanediamine) type complexes in the interesting region of 800—950 cm^{-1} must be considered to divide into the following three categories in relation to their chelate ring structure:

1. If two clear peaks appear in the 870—970 cm^{-1} region, the complex is in a centrosymmetric two-chair structure (C_{2h} point symmetry).
2. If three distinct peaks appear in this region, the complex is in a one-chair and one-skewboat structure (C_1 symmetry).
3. If the IR spectrum appears in a very complicated split pattern, even though a mutual exclusion is present in the IR and Raman spectroscopies, we must first refer to the experimentally confirmed case of the present study, in which the unit cell of the crystal lattice contains crystallographically non-equivalent plural complex species; even though all of them have two-chair rings, and are in the highest symmetry of C_{2h}, their ring structures are appreciably different regarding the dihedral angles of α and β.

If the complex has no inversion center and a lower symmetry than C_{2h} in a particular crystal lattice, the IR spectrum is expected to have a complicated pattern. However, there has been no (experimentally confirmed) example assignable to this situation (for *trans*-diacidobis(1,3-propanediamine)-type complexes). Further, we have not experienced a case in which both rings are in the skewboat form.

Conclusion

We have synthesized a new cyano–ammine complex of Rh(III) containing 1,3-propanediamine, *trans*-$[\mathrm{Rh(CN)_2(tn)_2}]^+$, and characterized the IR, Raman, UV, and $^{13}\mathrm{C}$ NMR data. X-Ray crystal-structure analyses identified very discrete complex cations of the two-chair structure having an inversion symmetry in the nitrate, perchlorate, and chloride crystal lattices. The IR splitting of the ν (C≡N) stretching band observed for the perchlorate was ascribed to the presence of two complex cations having fairly different Rh–C≡N angles in the lattices. On the basis of a normal coordinate analysis, the detailed IR behaviors in the 870—970 cm^{-1} region could be discussed in relation to their differences in structure, especially, concerning the two dihedral angles defined in the chelate rings.

It is expected that the present crystal compounds are able to be suitable host lattices for high-resolution absorption and luminescence spectroscopy of the corresponding Co(III) and Cr(III) complexes.

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