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Preparations, Properties, and Crystal Structures of *trans*-$[\mathrm{Rh(CN)_2(NH_3)_4}]\mathrm{Cl\cdot H_2O}$ and *trans*-$[\mathrm{Rh(CN)_2(en)_2}]\mathrm{Cl}$

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Syntheses of the title new complex compounds of Rh(III) were successful. Single, sharp IR peaks of ν (C≡N) were observed at 2130 $\mathrm{cm^{-1}}$ (*trans*-$[\mathrm{Rh(CH)_2(NH_3)_4}]\mathrm{Cl\cdot H_2O}$) and 2170 $\mathrm{cm^{-1}}$ (*trans*-$[\mathrm{Rh(CN)_2(en)_2}]\mathrm{Cl}$), respectively. The values of the ligand field tetragonal parameter D_t were estimated to be -366 and $-377\ \mathrm{cm^{-1}}$, respectively, based on the $^1E_g{}^a\,(D_{4h})\leftarrow{}^1A_{1g}$ transition (37100 $\mathrm{cm^{-1}}$: *trans*-$[\mathrm{Rh(CN)_2(NH_3)_4}]^+$; 37000 $\mathrm{cm^{-1}}$: *trans*-$[\mathrm{Rh(CN)_2(en)_2}]^+$). The X-ray crystal data are: for *trans*-$[\mathrm{Rh(CN)_2(NH_3)_4}]\mathrm{Cl\cdot H_2O}$, orthorhombic, *Cmcm*, a=7.961(3), b=17.295(2), c=7.436(3) Å, D_c=1.79, D_m=1.79 g cm^{-3}, Z=4; for *trans*-$[\mathrm{Rh(CN)_2(en)_2}]\mathrm{Cl}$, monoclinic, $P2_1/n$, a=9.665(4), b=9.107(3), c=6.779(3) Å, β=109.68(2)°, D_c=1.85, D_m=1.83 g cm^{-3}, Z=2. The N≡C–Rh–C≡N sequence of *trans*-$[\mathrm{Rh(CN)_2(NH_3)_4}]^+$ lies in a line of $m2m$ symmetry in the crystal. The central Rh atom of *trans*-$[\mathrm{Rh(CN)_2(en)_2}]^+$ occupies the special position of inversion symmetry. The important geometrical data of the complexes are Rh–N=2.07(1), Rh–C=2.02(3) Å, N–Rh–N=88.0(5)° (*trans*-$[\mathrm{Rh(CN)_2(NH_3)_4}]^+$) and Rh–N=2.080(3), 2.072(3), Rh–C=2.047(4) Å, N–Rh–N (within chelate ring)=82.7(1)° (*trans*-$[\mathrm{Rh(CN)_2(en)_2}]^+$).

A variety of Rh(III) complex compounds have been prepared and studied regarding their spectroscopic properties[1)] and kinetic mechanisms of photochemical reactions.[2)] However, investigations have not been developed to include the structurally rather familiar complexes of *trans*-$[\mathrm{Rh(CN)_2N_4}]^+$ ($\mathrm{N_4}$: $\mathrm{(NH_3)_4}$, $\mathrm{(en)_2}$, $\mathrm{(tn)_2}$), since synthetic methods have not yet been established.

Here, we report on the syntheses, spectroscopic identification, and X-ray crystal structures of the title new complex compounds of Rh(III).

Experimental

Preparation. ***trans*-$[\mathrm{Rh(CN)_2(NH_3)_4}]\mathrm{Cl\cdot H_2O}$.** Five grams of *trans*-$[\mathrm{Rh(CN)Cl(NH_3)_4}]\mathrm{Cl\cdot 1.5H_2O}$[3)] and 3.0 g of NaCN in 300 ml DMSO were heated at 85 °C for 1.5 h. A crude product which precipitated was collected by filtration and washed by ethanol and air-dried (2.8 g). This was dissolved in 100 ml $\mathrm{H_2O}$ and, after filtration, pure chloride was obtained upon the addition of concd HCl. Yield. 2.5 g (50%). Found: C, 8.60; H, 5.09; N, 30.06%. Calcd for $[\mathrm{Rh(CN)_2(NH_3)_4}]\mathrm{Cl\cdot H_2O}=\mathrm{C_2H_{14}N_6OClRh}$: C, 8.68; H, 5.10; N, 30.39%. The water of crystallization was easily lost in air at room temperature. An elemental analysis was also performed for the anhydrate. Found, 9.24; H, 4.37; N, 32.38%. Calcd for $[\mathrm{Rh(CN)_2(NH_3)_4}]\mathrm{Cl}=\mathrm{C_2H_{12}N_6ClRh}$: C, 9.29; H, 4.68; N, 32.51%.

***trans*-$[\mathrm{Rh(CN)_2(NH_3)_4}](\mathrm{ClO_4})$.** The immediate crystallization of the perchlorate occured when perchloric aicd was poured into an equeous solution of the chloride. Found: C, 7.49; H, 3.83; N, 25.98%. Calcd for $[\mathrm{Rh(CN)_2(NH_3)_4}](\mathrm{ClO_4})=\mathrm{C_2H_{12}N_6O_4ClRh}$: C, 7.45; H, 3.75; N, 26.06%.

***trans*-$[\mathrm{Rh(CN)Cl(en)_2}](\mathrm{ClO_4})$.** To an aqueous solution (500 ml) containing 6.0 g of *trans*-$[\mathrm{RhCl_2(en)_2}](\mathrm{NO_3})$,[4)] 6.0 g of $\mathrm{Na_2SO_3}$ was added. After the solution was heated to 80 °C, 3.0 g of NaCN was added. The characteristic yellow color of the starting dichlorocomplex was soon lost. After being cooled to room temperature, the solution was passed through a columun of anion-exchange resin ($\mathrm{Cl^-}$ form, MCL GEL CA08P), followed by a cation columun ($\mathrm{Li^+}$ form, Dowex 50-X8). Complete evaporation of the solution left a white powder (*trans*-$[\mathrm{Rh(CN)(SO_3)(en)_2}]$+LiCl). The obtained cyanosulfitocomplex was easily converted to the cyanochlorocomplex by treatment with concd HCl (20 ml) at 60 °C. Within ten minutes, when $\mathrm{SO_2}$ gas evolution ceased, to the resultant clear solution* 50 ml perchloric acid (70%) was added by ice cooling to give a mixture of solid $\mathrm{LiClO_4}$ and a white crystalline powder, which was collected on a filter and washed by ethanol to remove $\mathrm{LiClO_4}$ (the suction flask should be emptied before ethanol washing!) and air dried. Yield. 1.0 g (15%). Found: C, 15.38; H, 4.25; N, 18.07%. Calcd for $[\mathrm{Rh(CN)Cl(en)_2}](\mathrm{ClO_4})=\mathrm{C_5H_{16}N_5OCl_2Rh}$: C, 15.46; H, 4.20; N, 18.24%.

*Sometimes a mixture of *trans*-$[\mathrm{Rh(CN)Cl(en)_2}]\mathrm{Cl}$ and LiCl was precipitated at this stage. This was filtered and redissolved in water; perchloric acid was then added to convert to the perchlorate.

***trans*-$[\mathrm{Rh(CN)_2(en)_2}]\mathrm{Cl}$.** One gram of *trans*-$[\mathrm{Rh(CN)Cl(en)_2}](\mathrm{ClO_4})$ and 1.5 g of NaCN were mixed in 25 ml DMSO. The produced white precipitate was filtered, washed by ethanol and air-dried (*trans*-$[\mathrm{Rh(CN)Cl(en)_2}](\mathrm{CN})$, 0.7 g). This was suspended in 25 ml DMSO–$\mathrm{H_2O}$ (10:1 in volume ratio) medium. After the addition of 1.5 g of NaCN, the mixture was heated to 90 °C for 2 h. The obtained white solid was collected, washed by ethanol and dried. This was dissolved in 7 ml of $\mathrm{H_2O}$ and filtered once (if the solution is alkaline, acidify by concd HCl. Warning! HCN gas evolved). The addition of ethanol caused the precipitation of white crystalline powder. This was adsorbed on a cation-exchange columun ($\mathrm{Li^+}$ form, Dowex 50-X8) and eluted by 0.2 mol dm^{-3} LiCl. From the concentrated solution a white crystalline powder was separated, filtered, washed with ethanol. Yield 0.5 g (62%). Found: C, 23.34; H, 5.40; N, 27.44%. Calcd for $[\mathrm{Rh(CN)_2(en)_2}]\mathrm{Cl}=\mathrm{C_6H_{16}N_6ClRh}$: C, 23.19; H, 5.19; N, 27.06%.

***trans*-$[\mathrm{Rh(CN)_2(en)_2}](\mathrm{ClO_4})$.** A white crystalline powder of the perchlorate was obtained by the addition of perchloric acid (70%) to the above-mentioned filtrate, or an aqueous solution of the chloride. Found: C, 19.43; H, 4.58; N, 22.70%. Calcd for $[\mathrm{Rh(CN)_2(en)_2}](\mathrm{ClO_4})=\mathrm{C_6H_{16}N_6O_4ClRh}$: C, 19.22;

H, 4.31; N, 22.44%.

Spectroscopic Measurements and Thermogravimetric Measurement. IR, Raman, and UV spectroscopies were performed using a Perkin–Elmar 1600 FTIR spectrometer, a Jobin–Yvon Ramanor 1000 monochromator equipped with an NEC GLG3300 laser (Ar^+: 5145 Å), and a Hitachi U-3400 spectrometer, respectively. The Raman apparatus was also employed for luminescence measurements by excitation of the 312 nm line of a high-pressure mercury lamp. ^1H and ^{13}C NMR measurements were accomplished by a JOEL GSX 400 spectrometer. A TGA curve was taken with a Shinkuriko TGD-7000 RH thermogravimeter.

X-Ray Crystal Structure Analyses. X-Ray crystallographic studies were carried out using a Rigaku AFC-5 four-circle automated diffractometer. Graphite monochromated Mo $K\alpha$ (λ=0.71073 Å) was used as the X-ray source. A crystal of *trans*-$[Rh(CN)_2(NH_3)_4]Cl\cdot H_2O$ was sealed into a silica glass capillary (ϕ=0.7 mm). Experimental details, crystallographic data and the R factors of the final refinements are shown in Table 1. All computational studies were carried out on a FACOM M760 computer at the Computer Center of Rikkyo University, using universal X-ray crystal structure analysis program (UNICSIII, MULTAN, ORTEP).[5] An absorption correction was employed (North et al.[6]). The atomic scattering factors were taken from "International Tables for X-Ray Crystallography," Vol. IV, Kynoch Press, Birmingham (1974). The initial phases of the structure factor determined by a direct method were refined by cycles of a block-matrix least-square method. The positions of the hydrogen atoms were obtained by difference-Fourier syntheses. The final full-matrix treatments sufficiently decreased the R factors (Table 1).

The position of the water of crystallization of *trans*-$[Rh(CN)_2(NH_3)_4]Cl\cdot H_2O$ was not clearly revealed on the difference-Fourier maps. If an oxygen atom was placed at a special position ($2/m$, multiplicity: 0.25) of (0.5, 0, 0), for which the maximum residual electron density (1.86 e Å^{-3}) was yielded, a rather large value of the isotropic temperature factor was obtained after a sufficient number of cycles of a least-square treatment. However, this point is recognized as being a vacant hole in the crystal; the shortest contact distance from this point to a non-hydrogen atom is 3.54 Å (to N(1) of the complex cation). The TGA curve indicated a weight loss corresponding to ca. 1 mol of crystallization water below 60 °C. It is therefore believed that almost all of the water molecules were lost from this point before the X-ray study, although the sample crystal was sealed into a small capillary. The observed density (1.77 g cm^{-3}) of the freshly prepared crystal is slightly smaller than the calculated value (1.79 g cm^{-3}), based on monohydrated stoichiometry.

Tables of the observed and calculated structure factors are deposited as Document No. 9105 at the Office of the Editor of Bull. Chem. Soc. Jpn.

Results and Discussion

Baranovskii et al.[7,8] and Skibsted et al.[9] have reported the syntheses of several cyanoammine complexes of Rh(III), which involve $[Rh(CN)(NH_3)_5]Cl_2$, *trans*-$[Rh(CN)(SO_3)(NH_3)_4]\cdot 2H_2O$, *trans*-$[Rh(CN)Cl(NH_3)_4]Cl$, and $[Rh(CN)_3(NH_3)_3]$. However, Baranovskii et al.[12] have mentioned that an attempt to introduce a second CN^- to *trans*-$[Rh(CN)(SO_3)(NH_3)_4]$ with excess CN^- was not successful in an aqueous solution. Subsequently, Kane-Maguire et al.[10] synthesized *trans*-$[Rh(CN)_2(cyclam)](ClO_4)$ by a reaction of the corresponding dichlorocomplex and CN^- in an aqueous solution. A direct synthesis[11,12] of *trans*-

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

	trans-$[Rh(CN)_2(NH_3)_4]Cl\cdot H_2O$	*trans*-$[Rh(CN)_2(en)_2]Cl$
Formula	$RhC_2N_6H_{14}OCl$	$RhC_6N_6H_{16}Cl$
F. W.	276.54	310.59
Crystal system	Orthorhombic	Monoclinic
Space group	*Cmcm*	$P2_1/n$
a/Å	7.961(3)	9.665(4)
b/Å	17.295(2)	9.107(3)
c/Å	7.436(3)	6.779(3)
β/degree		109.68(2)
V/Å^3	1023.8(6)	561.8(4)
Z	4	2
D_x/g cm^{-3}	1.79	1.85
D_m/g cm^{-3}	1.77	1.83
μ(Mo$K\alpha$)/cm^{-1}	18.6	17.1
Crystal size/mm	0.43×0.20×0.15	0.48×0.35×0.10
Scan mode	$\omega(2\theta\leqq25°)$, ω-$2\theta(25°<2\theta\leqq55°)$	$\omega(2\theta\leqq25°)$, ω-$2\theta(25°<2\theta\leqq55°)$
Scan width/deg	1.2+0.5tan θ	1.2+0.5tan θ
Scan speed/deg min^{-1}	4	4
No. of refl. measd.	1092	1868
No. of unique refl. with $F_o\geqq3\sigma(F_o)$	970	1375
Max. min. residual electron density/(e Å^{-3})	1.86, −0.82	1.00, −1.46
Max (shift/esd)	0.29	0.22
Weighting scheme	Unit weight	Unit weight
R	0.0442	0.0289
R_w	0.0804	0.0315

$[Co(CN)_2(N)_4]^+$ ($(N)_4$: $(NH_3)_4$, $(en)_2$, $(tn)_2$) from the corresponding dichlorocomplex is also possible in DMSO or a methanol medium.

We first studied the direct reaction of *trans*-$[RhCl_2(NH_3)_4]Cl$ and NaCN under various conditions (concentrations, temperatures, and media). However, this reaction yielded only uncharacterizable insoluble solids, even in cases where the reaction occured.

For the corresponding Co(III) complex, Maki et al.[13] employed the reaction of *trans*-$[Co(CN)Cl(NH_3)_4]Cl+NaCN$ to obtain *trans*-$[Co(CN)_2(NH_3)_4]$ in DMSO. Therefore, we have studied this type of reaction, i.e., *trans*-$[Rh(CN)Cl(N)_4]Cl+NaCN$ ($(N)_4$: $(NH_3)_4$, $(en)_2$), in DMSO. It was found that, while the ligand substitution of Cl^- by CN^- hardly proceeded in a pure DMSO medium, especially for the ethylenediamine complex, the reaction easily occured in a DMSO–H_2O mixed medium to give the desired *trans*-dicyano complex compounds (see experimental section). An attempt to synthesize the corresponding tn (1,3-propanediamine) complex, *trans*-$[Rh(CN)_2(tn)_2]^+$, is now proceeding using a similar ligand-substitution reaction in either a DMSO–H_2O or ethanol medium.

The IR and Raman spectra of the present Rh(III) complexes are very similar to the corresponding Co(III) complexes.[14—16] The numerical data are summerized in Table 2; some possible assignments are included. It was mentioned[13] in a study of the

Table 2. Principal IR and Raman Bands (cm^{-1}) of *trans*-$[Rh(CN)_2(NH_3)_4]Cl\cdot H_2O$ and *trans*-$[Rh(CN)_2(en)_2]Cl$

trans-$[Ph(CN)_2(NH_3)_4]^+$			*trans*-$[Rh(CN)_2(en)_2]^+$		
IR	Raman	Assignment[a]	IR	Raman	Assignment[a]
278		δ (N-Rh-N)		216	
283	285	δ (N-Rh-N)			
				253	δ (cycle)
387		δ (Rh-C≡N)		321	
	417	ν (Rh-C)	360		
456		ν (Rh-N)	390		
	478	ν (Rh-C)		421	ν (Rh-C)
	497	ν (Rh-N)	440		
824		ρ (Rh-NH_3)		453	
1310		δ_s (H-N-H)	486		ν (Rh-N)
1690		δ_a (H-N-H)	518		ν (Rh-C)
				542	δ N-Co-C
			582		δ N-C-C
2125		ν (C≡N)	2126		ν (C≡N)

a) Ref. 14—16.

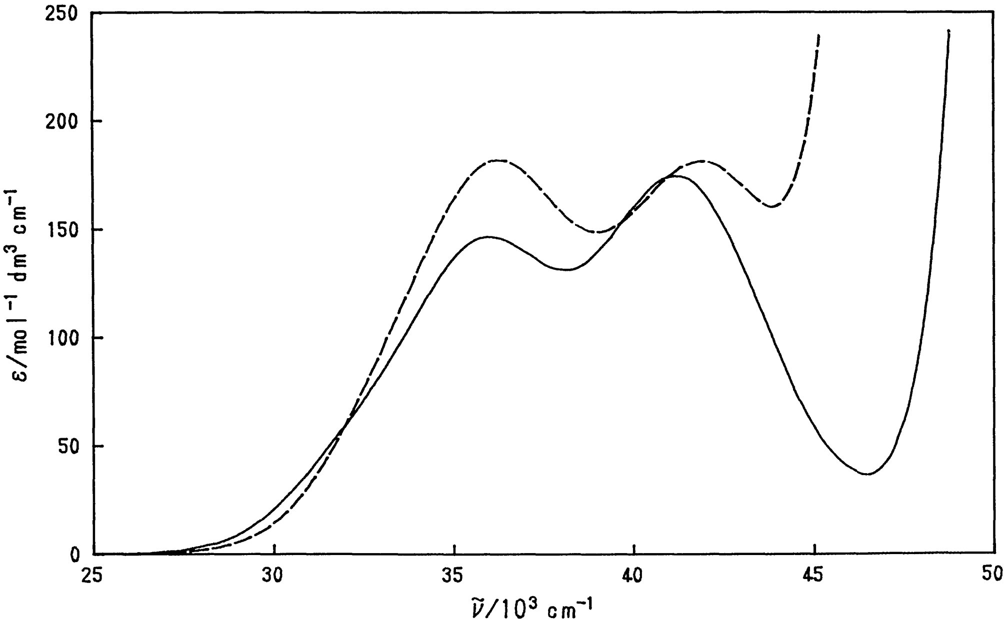


Fig. 1. Electronic absorption spectra of cyanoammine complexes of Rh(III) in aqueous solution. (a) —— *trans*-$[Rh(CN)_2(NH_3)_4]Cl\cdot H_2O$; (b) ----- *trans*-$[Rh(CN)_2(en)_2]Cl$.

corresponding Co(III) complexes that no splitting feature of the sharp IR line due to C≡N stretching vibration appeared between 2100—2200 $\mathrm{cm^{-1}}$ is diagnostic to the *trans*-isomer. In accord with this statement, the present *trans*-dicyano complexes of Rh(III) did not show any splitting of the C≡N band.

The UV absorption spectra were shown in Fig. 1, and the numerical data are summerized in Table 3, in which the ligand field assignments in the D_{4h} effective site symmetry are included. The lowest spin-allowed component of $^1A_{2g}(D_{4h})\leftarrow{}^1A_{1g}$ was not clearly observed for the present Rh(III) complexes compared to the corresponding Co(III) complexes.[14—16] If the energy of the $^1A_{2g}\leftarrow{}^1A_{1g}$ is approximated[17] to be that of the $^1T_{1g}(O_h)\leftarrow{}^1A_{1g}$ transition of $[\mathrm{Rh(NH_3)_6}]^{3+}$ (32800 $\mathrm{cm^{-1}}$) and/or $[\mathrm{Rh(en)_3}]^{3+}$ (33200 $\mathrm{cm^{-1}}$), the values of the tetragonal parameter, D_t, are estimated to be -366 $\mathrm{cm^{-1}}$ and -377 $\mathrm{cm^{-1}}$, respectively, for *trans*-$[\mathrm{Rh(CN)_2(NH_3)_4}]^+$ and *trans*-$[\mathrm{Rh(CN)_2(en)_2}]^+$.

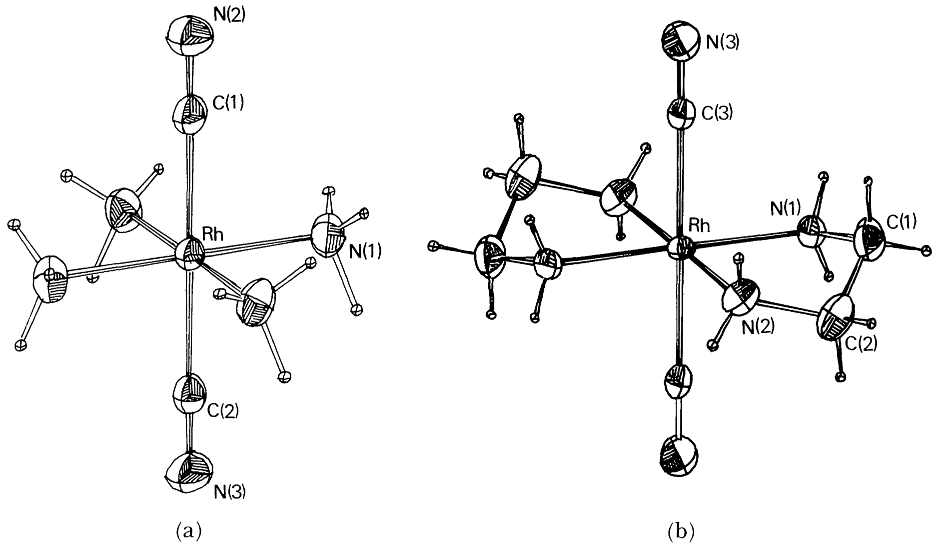
The present Rh(III) complexes exhibited a visible luminescence with ultraviolet irradiation (Hg 312 nm line). The band maxima of *trans*-$[\mathrm{Rh(CN)_2(NH_3)_4}]^+$ and *trans*-$[\mathrm{Rh(CN)_2(en)_2}]^+$ are located at 18300 $\mathrm{cm^{-1}}$ (10 K) and 17500 $\mathrm{cm^{-1}}$ (77 K), respectively. The band of *trans*-$[\mathrm{Rh(CN)_2(NH_3)_4}]^+$ showed a resolved vibrational fine structure at low temperatures. Details will be reported elsewhere.[18]

The ammine ^{1}H NMR signal was detected as a single peak at 3.5 ppm for *trans*-$[\mathrm{Rh(CN)_2(NH_3)_4}]\mathrm{Cl}$ (in D_2O) suggesting that all of the ammine ligands are magnetically equivalent in the *trans*-form. For *trans*-$[\mathrm{Rh(CN)_2(en)_2}]^+$, methylene and amido ^{1}H signals were observed at 2.8 and 5.1 ppm, respectively. It has been confirmed[19] that the methylene ^{1}H signal is a sharp singlet in *trans*-$[\mathrm{Co(CN)_2(en)_2}]^+$, while *cis*-$[\mathrm{Co(CN)_2(en)_2}]^+$, exhibits a complicated split pattern. The methylene ^{13}C NMR signal of *trans*-$[\mathrm{Rh(CN)_2(en)_2}]^+$ was quite normally identified as being a single peak at 48.9 ppm.[20] On the other hand, the cyano-carbon signal was clearly split into two components of nearly equal strength for the present complexes (at 140.3 and 140.6 ppm for *trans*-$[\mathrm{Rh(CN)_2(NH_3)_4}]^+$ and at 140.2 and 140.6 ppm for *trans*-$[\mathrm{Rh(CN)_2(en)_2}]^+$). This experimental finding must be further investigated regarding the solution chemistry of the *trans*-dicyano-type metal complexes.

The crystal structures of the present new complex compounds were determined. Of course, the well

Table 3. Ligand Field Absorption Bands ($\mathrm{cm^{-1}}$) of *trans*-$[\mathrm{Rh(CN)_2(NH_3)_4}]^+$, *trans*-$[\mathrm{Rh(CN)_2(en)_2}]^+$, and Related Complexes

Complex	I $^1E_g{}^a\leftarrow{}^1A_{1g}$	II $^1E_g{}^b\leftarrow{}^1A_{1g}$	Ref.
$[\mathrm{Rh(CN)(NH_3)_5}]^{2+}$	34800	40700	8
trans-$[\mathrm{Rh(CN)Cl(NH_3)_4}]^+$	33100	38600	8
trans-$[\mathrm{Rh(CN)Cl(en)_2}]^+$	33500	39000	This work
trans-$[\mathrm{Rh(CN)_2(NH_3)_4}]^+$	36000	41500	This work
trans-$[\mathrm{Rh(CN)_2(en)_2}]^+$	36500	42500	This work
trans-$[\mathrm{Rh(CN)_2(cyclam)}]^+$	37500	45900	10



(a) (b)

Fig. 2. ORTEP drawings of (a) *trans*-$[\mathrm{Rh(CN)_2(NH_3)_4}]^+$ and (b) *trans*-$[\mathrm{Rh(CN)_2(en)_2}]^+$ cations.

discrete complex cations in the *trans*-geometry were identified in both crystals (Fig. 2), being consistent with spectroscopic evidence. The positional parameters are summarized in Table 4. The bond distances and angles are included in Table 5, in which the reported values for *trans*-$[Co(CN)_2(en)_2](ClO_4)$ are also included.

In a crystal of *trans*-$[Rh(CN)_2(NH_3)_4]Cl\cdot H_2O$, the N≡C–Rh–C≡N molecular axis lies in a line with a special symmetry of $m2m$. The four N atoms of the ammonia ligands are required to form a rectangular plane perpendicular to the molecular axis. Therefore, the crystallographically required symmetry of the complex is C_{2v}. In the case of *trans*-$[Rh(CN)_2(en)_2]Cl$, the Rh atom occupies a special position with inversion symmetry. Therefore, the two Rh-en rings are in the $\delta\lambda$ conformation. The positional parameters of the complex (Table 4) indicate the C_{2h} effective point symmetry of the complex (all ∠C–Rh–N fall ca. 90° and all Rh–N fall ca. 2.07 Å). In comparision to the geometrical data of the corresponding Co(III) complex,[21] the Rh–C and Rh–N bonds are elongated by about 5%. This amount of the M–L bond length increase from the Co(III) complexes to the Rh(III) complexes is identical with that found in another comparison by Hambley et al.[22] On the other hand, the intra-ligand parameters of the en (N–C and C–C bond distances and N–C–C angles) are well retained in the Co(III) and Rh(III) complexes. This conservative nature of the intra-ligand structure of en accompanies a reduction of the ∠N–Rh–N chelate angles in the Rh(III) complex (82.7°), compared with those in the Co(III) complex (86.4°).

Table 4. Positional Parameters (×10⁴) of *trans*-$[Rh(CN)_2(NH_3)_4]\ Cl\cdot H_2O$ and *trans*-$[Rh(CN)_2(en)_2]Cl$

Atom	x/a	y/b	z/c	B_{eq}(Å^2)[a]
	trans-$[Rh(CN)_2(NH_3)_4]Cl\cdot H_2O$			
Rh	0	1417(1)	2500	1.7
Cl	−5000	2337(4)	2500	2.5
N(1)	−1809(18)	1416(8)	493(17)	2.7
N(2)	0	3252(16)	2500	3.4
N(3)	0	−403(16)	2500	3.8
C(1)	0	2588(17)	2500	2.5
C(2)	0	249(17)	2500	2.3
	trans-$[Rh(CN)_2(en)_2]Cl$			
Rh	0	5000	5000	1.3
Cl	0	0	5000	5.3
N(1)	817(3)	3246(3)	3764(5)	1.9
N(2)	2131(3)	5770(4)	5724(5)	2.2
N(3)	820(4)	3361(4)	9344(5)	3.3
C(1)	2444(4)	3325(5)	4568(7)	2.8
C(2)	2875(4)	4905(6)	4508(7)	3.0
C(3)	544(4)	3933(4)	7817(5)	1.9

a) The isotropic equivalent thermal parameters is given as $B_{eq}=4/3(\sum_i\sum_j B_{ij}\mathbf{a}_i\mathbf{a}_j)$.

Conclusion

Two new cyanoammine-rhodium(III) complexes, *trans*-$[Rh(CN)_2(NH_3)_4]^+$ and *trans*-$[Rh(CN)_2(en)_2]^+$, were synthesized in a DMSO–H_2O mixed medium. X-Ray crystal structure analyses of *trans*-$[Rh(CN)_2(NH_3)_4]Cl\cdot H_2O$ and *trans*-$[Rh(CN)_2(en)_2]Cl$ showed well discrete complex cations in *trans*-dicyano geometry. The UV, IR, Raman, ^{1}H- and ^{13}C NMR spectroscopic data were characterized.

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Table 5. Relevant Bond Distances (Å) and Angles (deg.) of *trans*-$[M(CN)_2N_4]^+$

	trans-$[Rh(CN)_2(NH_3)_4]^+$	*trans*-$[Rh(CN)_2(en)_2]^+$	*trans*-$[Co(CN)_2(en)_2]^{+}$[b]
M–C	2.02(3), 2.02(3)	2.047(4)	1.91(1)
M–N	2.07(1)	2.080(3), 2.072(3)	1.99(1), 1.99(1)
C≡N	1.15(4), 1.13(4)	1.109(5)	1.16(2)
N–C(en)		1.482(5), 1.488(6)	1.50(2), 1.49(2)
C–C		1.503(7)	1.54(2)
M–C≡N	180	179.0(4)	178.8(11)
N–M–C	90.1(4), 89.9(4)	89.9(1), 91.0(1)	90.0(4), 89.1(4)
N–M–N	92.0(5), 88.0(5)	82.7(1)[a]	86.4(4)[a]
M–N–C		108.3(2), 108.5(2)	108.1(7), 108.9(7)
N–C–C		107.9(3), 107.6(4)	107.1(10), 107.1(10)

a) In chelate. b) Ref. 21.

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