# The Crystal and Molecular Structure of *cis*-Dichloro[3,11-dimethyl-3,11,17,18-tetraazatricyclo[11.3.1.1$^{5,9}$]octadeca-1(17),5,7,9(18),13,15-hexaene]rhodium(III) Cation

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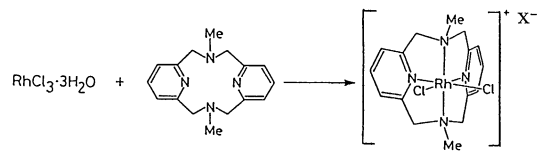
**Synopsis.** The crystal and molecular structure of the title compound has been determined by the use of the X-ray diffraction method. The central metal atom coordinates all four of the nitrogen atoms of *N,N'*-dimethyl 2,11-diaza[3.3](2,6)-pyridinophane and two additional chloride atoms in an approximately octahedral geometry.

The chemical and spectroscopic studies of rhodium(III) complexes of tetraaza macrocyclic ligands such as 12-membered 1,4,7,10-tetraazacyclododecane (cyclen),[1a,d,e] or 14-membered 1,4,8,11-tetraazacyclotetradecane (cyclam)[1b-e] have frequently been reported. In addition, the results of a crystallographic investigation of *cis*-[Rh(cyclam)Cl$_2$]Cl have also appeared.[2] However, little is known about the metal complexes of metapyridophane ligands composed of a somewhat smaller sized ring than cyclam. Most of the 2,11-diaza[3.3](2,6)pyridophanes[3] are known to have a *syn*-conformation, even in solution.[4] The restricted flexibility in the conformational behavior as well as a small concave cavity in the coordination sites of the ligand system are expected to have a significant influence on the ligating ability and geometries of the metal complexes. Recently, the crystal structure of a copper(II) complex of *N,N'*-dimethyl 2,11-diaza-[3.3](2,6)-pyridophane **1**[3] has been reported.[5] This paper will report on the synthesis and X-ray crystal structure analysis of a rhodium(III) complex of the same pyridinophane ligand **1**, 3,11-dimethyl-3,11,17,18-tetraazatricyclo[11.3.1.1$^{5,9}$]octadeca-1(17),5,7,9(18),13,15-hexaene.




**1** **2a** X=$BF_4$
**2b** X=$BPh_4$
**2c** X=$PF_6$

## Experimental

**Synthesis of Dichloro[(3,11-dimethyl-3,11,17,18-tetraazatricyclo[11.3.1.1$^{5,9}$]octadeca-1(17),5,7,9(18),13,15-hexaene]rhodium(III) Tetrafluoroborate 2a, Tetraphenylborate 2b, and Hexafluorophosphate 2c.** A solution of **1**[4d] (268 mg, 1.0 mmol) and $RhCl_3 \cdot 3H_2O$ (263 mg, 1.0 mmol) in methanol (10 cm$^3$) was heated at 80 °C for 2h. The filtration of the resultant yellow solution, followed by treatment with a hot methanolic solution (5 cm$^3$) of $NaBF_4$ (132 mg, 1.2 mmol), produced crystals of **2a**; these crystals were then recrystallized from $CH_3CN$-benzene (487 mg, 0.92 mmol, 92%). Found: C, 36.24; H, 3.68; N, 10.74; Cl, 13.67%. Calcd for $C_{16}H_{20}BCl_2N_4F_4Rh$: C, 36.33; H, 3.81; N, 10.59; Cl, 13.40%. $^1$H NMR ($CDCl_3$) $\delta$=3.29 (6H, s), 4.80 (8H, ABq, $J$=16.7 Hz), 7.39 (4H, d, $J$=7.9 Hz), 7.14 (2H, dd, $J$=6.6, 8.4 Hz); $^{13}$C NMR ($CDCl_3$) $\delta$=53.7 (q), 74.9 (t), 122.9 (d), 141.2 (d), 158.4 (s).

The other compounds, **2b** and **2c**, were prepared and purified in a similar way except for using $NaBPh_4$ and $NH_4PF_6$ respectively instead of $NaBF_4$.

**2b.** Yield (96%). Found: C, 62.69; H, 5.33; N, 8.94%. Calcd for $C_{40}H_{40}BCl_2N_4Rh \cdot CH_3CN$: C, 62.86; H, 5.40; N, 8.73%.

**2c.** Yield (90%). Found: C, 32.80; H, 3.32; N, 9.78%. Calcd for $C_{16}H_{20}Cl_2F_6N_4PRh$: C, 32.73; H, 3.43; N, 9.54%.

The $^1$H and $^{13}$C NMR spectra were recorded at 90 MHz by using a Hitachi R-90H FT-NMR spectrometer, with $Me_4Si$ as the internal standard. Microanalyses were performed by the Instrumental Analysis Center for Chemistry, Faculty of Science, Tohoku University.

**Crystal-Structure Determination of 2b.** Crystal data of **2b**.[6] $C_{40}H_{40}BCl_2N_4Rh \cdot CH_3CN$, M=802.46, monoclinic, space group $P2_1/n$, $a$=28.055(9), $b$=9.066(2), $c$=15.552(3) Å, $\beta$=75.27(2)°, $V$=3825.6(17) Å$^3$, $Z$=4, $D_{calcd}$=1.394 g cm$^{-3}$, $\mu$(Mo-$K\alpha$)=2.032 cm$^{-1}$. A yellow crystal with approximate dimensions of 0.25×0.25×0.25 mm was used for data measurement on a Rigaku AFC-5R automatic four-circle diffractometer (AFC-5PR), using graphite-monochromated Mo-$K\alpha$ radiation ($\lambda$=0.71069 Å). The unit-cell parameters were obtained by a least squares refinement of the angular setting of 25 high-angle ($2\theta \approx 30°$) reflections. A total of 7557 independent reflections within $2\theta$=52° were collected using the $\theta$–$2\theta$ scan mode. The position of the Rh atom was determined by the direct method, while the remaining non-hydrogen atoms were located step by step, by difference Fourier syntheses; then, all the non-hydrogen atoms were refined by the use of anisotropical temperature factors. Some of the hydrogen atoms were found on the difference map experimentally, but the other parameters were calculated geometrically except for the solvent acetonitrile molecule. The parameters of hydrogen atoms were included in the refinement with isotropic temperature factors by the use of the block-diagonal least-squares method.

The final $R$ value was 0.049 ($R_w$=0.055) for 5199 reflections with $F_o > 3\sigma(F_o)$ All the calculations were carried out on a ACOS 2000 at the Computer Center of Tohoku University, using a local version of the UNICS III programs.[7] The scattering factors were taken from Ref 8.

## Results and Discussion

A perspective drawing of the cationic complex **2b** is shown in Fig. 1, while selected bond lengths and bond angles are listed in Table 1. The cationic complex has a pseudo-octahedral geometry, with the coordination of all four nitrogen donors of the cyclic ligand and the two chloride ligands to the Rh(III) center, as shown in Fig. 1.

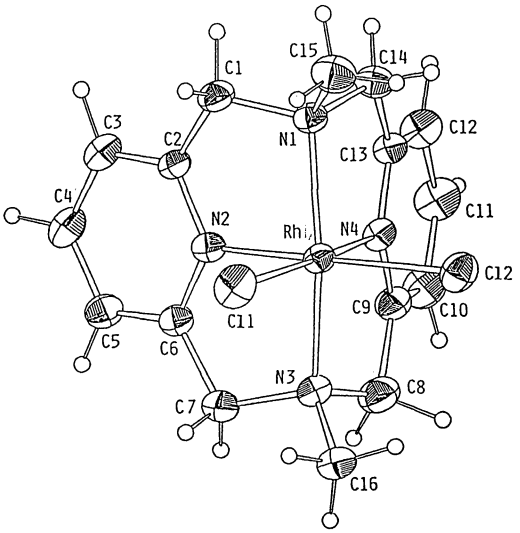



Fig. 1. ORTEP drawing of the cationic complex **2b**.

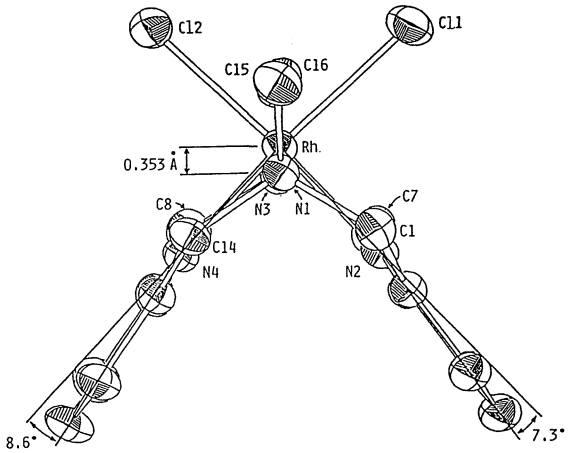



Fig. 2. Side view of **2b** projected along the N(1)-N(3) axis.

Table 1. Selected Bond Lengths and Bond Angles, with Estimated Standard Deviations in Parentheses

| | | | |
|---|---|---|---|
| (a) Bond length/Å | | | |
| Rh-Cl(1) | 2.353(2) | N(4)-C(9) | 1.333(8) |
| Rh-Cl(2) | 2.349(2) | N(4)-C(13) | 1.339(7) |
| Rh-N(1) | 2.094(5) | C(1)-C(2) | 1.473(9) |
| Rh-N(2) | 1.958(5) | C(2)-C(3) | 1.377(9) |
| Rh-N(3) | 2.099(5) | C(3)-C(4) | 1.387(10) |
| Rh-N(4) | 1.960(5) | C(4)-C(5) | 1.381(10) |
| N(1)-C(1) | 1.508(8) | C(5)-C(6) | 1.367(9) |
| N(1)-C(14) | 1.517(8) | C(6)-C(7) | 1.496(9) |
| N(1)-C(15) | 1.494(9) | C(8)-C(9) | 1.517(10) |
| N(2)-C(2) | 1.344(7) | C(9)-C(10) | 1.372(10) |
| N(2)-C(6) | 1.344(7) | C(10)-C(11) | 1.376(11) |
| N(3)-C(7) | 1.509(9) | C(11)-C(12) | 1.378(10) |
| N(3)-C(8) | 1.488(10) | C(12)-C(13) | 1.381(9) |
| N(3)-C(16) | 1.486(10) | C(13)-C(14) | 1.495(8) |
| (b) Bond Angles/° | | | |
| Cl(1)-Rh-Cl(2) | 94.8(1) | C(7)-N(3)-C(16) | 108.2(5) |
| Cl(1)-Rh-N(1) | 95.8(1) | C(8)-N(3)-C(16) | 108.4(5) |
| Cl(1)-Rh-N(2) | 89.1(1) | Rh(1)-N(4)-C(9) | 118.4(4) |
| Cl(1)-Rh-N(3) | 96.8(1) | Rh(1)-N(4)-C(13) | 117.3(3) |
| Cl(1)-Rh-N(4) | 174.9(1) | C(9)-N(4)-C(13) | 123.0(5) |
| Cl(2)-Rh-N(1) | 97.2(1) | N(1)-C(1)-C(2) | 113.1(5) |
| Cl(2)-Rh-N(2) | 175.9(1) | N(2)-C(2)-C(1) | 113.5(5) |
| Cl(2)-Rh-N(3) | 96.1(1) | N(2)-C(2)-C(3) | 118.9(5) |
| Cl(2)-Rh-N(4) | 90.1(1) | C(1)-C(2)-C(3) | 127.3(5) |
| N(1)-Rh-N(2) | 82.9(1) | C(2)-C(3)-C(4) | 118.9(5) |
| N(1)-Rh-N(3) | 160.6(2) | C(3)-C(4)-C(5) | 120.5(6) |
| N(1)-Rh-N(4) | 83.4(1) | C(4)-C(5)-C(6) | 119.2(6) |
| N(2)-Rh-N(3) | 82.7(2) | N(2)-C(6)-C(5) | 119.0(5) |
| N(2)-Rh-N(4) | 85.8(1) | N(2)-C(6)-C(7) | 113.2(5) |
| N(3)-Rh-N(4) | 82.5(2) | C(5)-C(6)-C(7) | 127.4(5) |
| Rh-N(1)-C(1) | 105.4(3) | N(3)-C(7)-C(6) | 112.4(5) |
| Rh-N(1)-C(14) | 106.2(3) | N(3)-C(8)-C(9) | 112.2(6) |
| Rh-N(1)-C(15) | 116.9(3) | N(4)-C(9)-C(8) | 113.1(5) |
| C(1)-N(1)-C(14) | 110.6(4) | N(4)-C(9)-C(10) | 119.3(6) |
| C(1)-N(1)-C(15) | 109.4(4) | C(8)-C(9)-C(10) | 127.2(6) |
| C(14)-N(1)-C(15) | 107.9(4) | C(9)-C(10)-C(11) | 119.1(7) |
| Rh-N(2)-C(2) | 117.7(3) | C(10)-C(11)-C(12) | 120.4(7) |
| Rh-N(2)-C(6) | 118.2(3) | C(11)-C(12)-C(13) | 118.5(6) |
| C(2)-N(2)-C(6) | 123.5(4) | N(4)-C(13)-C(12) | 119.3(5) |
| Rh-N(3)-C(7) | 106.1(4) | N(4)-C(13)-C(14) | 114.3(5) |
| Rh-N(3)-C(8) | 106.9(4) | C(12)-C(13)-C(14) | 126.0(5) |
| Rh-N(3)-C(16) | 115.8(4) | N(1)-C(14)-C(13) | 112.3(4) |
| C(7)-N(3)-C(8) | 111.2(5) | | |

The tertiary nitrogen donors, N(1) and N(3), occupy the axial sites of the octahedral arrangement, while two pyridine nitrogen atoms, N(2) and N(4), and the two chloro ligands, Cl(1) and Cl(2), form the equatorial plane, which is almost planar with a deviation of less than 0.007 Å. However, the several distortions from the ideal octahedral geometry may be illustrated as follows. The N(2)-Rh-N(4) angle is reduced to 85.8(1)°, while the Cl(1)-Rh-Cl(2) angle is expanded to 94.8(1)°. The N(1)-Rh-N(3) (160.6(2)°) bond angle indicates that the Rh atom deviates 0.353 Å from the N(1)-N(3) axis, jutting out from the cavity of the cyclic ligand, as can be seen in the side view of the molecular structure (Fig. 2). Furthermore, the two pyridine planes, being planar within the limits of experimental error, are bent toward the bisectional axis of the coordination angle, N(2)-Rh-N(4), to the extent of 8.6° and 7.3°.

The reported bond angles, N(2)-Rh-N(4), Cl(1)-Rh-Cl(2), and N(1)-Rh-N(3), of the cyclam complex are 94.3°, 88.3°, and 173.0° respectively, near the normal octahedral geometry.[2] The replacement of the N(2) and N(4) of the cyclam ligand by the pyridine nitrogens of **1** does not much decrease the Rh-Cl(1) and Rh-Cl(2) bond lengths, which function as probes of the *trans*-effect of these nitrogens, but it does reduce the Rh-N(2) and Rh-N(4) bond lengths to less than 1.96 Å.

Fronczek et al. proposed that the small ring sized and reduced flexibility of the ligand **1** did not permit the coplanar coordination of the four nitrogen atoms, and they reported that the copper complex of **1** was in a highly distorted octahedral arrangement.[5]

The oxidation number of the Rh(III) cation is greater than that of the Cu(II) cation, while the d electrons belonging to Rh(III) are fewer than those belonging to Cu(II). It thus appears that the Rh(III) cation tends to coordinate all four N atoms of **1** as nearly as possible, overcoming the restricted flexibility

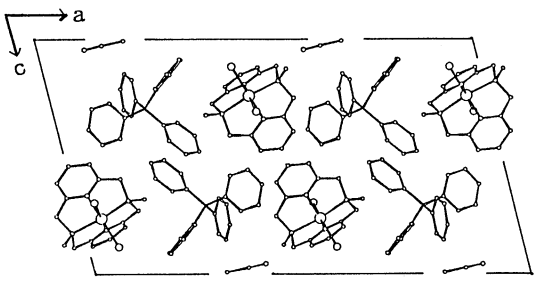



Fig. 3. Crystal structure view along the b axis.

of the ligand. This tendency may then force the complex **2** to be close to the normal octahedral geometry. The angles of both the axial N(1)-Rh-N(3) (160.6°) and the equatorial N(2)-Rh-N(4) (85.8°) of **2b** are greater than the corresponding angles, N(1)-Cu-N(3) (147.8°) and N(2)-Cu-N(4) (78.9°) respectively, of the copper complex.[5]

The comparison of the $^{1}H$ and $^{13}C$ NMR spectra of **2a** and **2c** with those of **2b** suggests that the cations of **2a** and **2c** have the same octahedral type arrangement.

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