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Preparation and Characterization of T-Cage-Type S-Bridged $Rh^{III}Cd^{II}$ Polynuclear Complexes with 2-Aminoethanethiolate

Takumi KONNO,* Yuichi KAGEYAMA, and Ken-ichi OKAMOTO
Department of Chemistry, University of Tsukuba, Tsukuba, Ibaraki 305

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Synopsis. The reaction of *fac(S)*-[Rh(aet)$_3$] with Cd(NO$_3$)$_2$ in water gave a T-cage-type S-bridged $Rh^{III}{}_4Cd^{II}{}_3$ complex with a "defective" $[Cd_3HO]^{5+}$ core, [{Rh(aet)$_3$}$_4$Cd$_3$HO](NO$_3$)$_5$ (**1**). The corresponding T-cage-type $Rh^{III}{}_4Cd^{II}{}_4$ complex with a "complete" $[Cd_4O]^{6+}$ core, [{Rh(aet)$_3$}$_4$Cd$_4$O](NO$_3$)$_6$ (**2**), was formed by the reaction of *fac(S)*-[Rh(aet)$_3$] with a mixture of Cd(NO$_3$)$_2$ and CdO in water. These complexes were characterized by a combination of X-ray diffraction and spectroscopic methods.

While it has been recognized that *fac(S)*-[M(aet)$_3$] or *fac(S)*-[M(L-cys-*N,S*)$_3$]$^{3-}$ (M=Co^{III}, Rh^{III}, or Ir^{III}, aet=2-aminoethanethiolate, and L-cys=L-cysteinate) readily react with a variety of metal ions to form S-bridged polynuclear complexes, the linear-type trinuclear structure in $[M'\{M(\text{aet or L-cys-}N,S)_3\}_2]^{n+\text{ or }n-}$ (M′ is an octahedral metal ion such as Fe^{III}, Co^{III}, or Ni^{II}) has long been the only S-bridged polynuclear structure which has been well characterized.[1—8] We have recently found that the reactions of *fac(S)*-[M(aet)$_3$] with tetrahedral Zn^{II} produce a new class of T-cage-type S-bridged octanuclear complexes with a "complete" $[Zn_4O]^{6+}$ core, $[\{M(aet)_3\}_4Zn_4O]^{6+}$, by way of heptanuclear compexes with a "defective" $[Zn_3HO]^{5+}$ core, $[\{M(aet)_3\}_4Zn_3HO]^{5+}$.[9,11—13] Furthermore, the linear-type trinuclear structure in $[Co\{M(aet)_3\}_2]^{3+}$ (M=Rh^{III} or Ir^{III}) was found to be convertible into the T-cage-type structure in $[\{M(aet)_3\}_4Zn_xCo_{4-x}O]^{6+}$ (x=3.7 for M=Rh^{III} and x=2.8 for M=Ir^{III}), by substitution of the bridging Co^{III} with Zn^{II}.[10,13] From these results it was postulated that the T-cage-type structure is formed from *fac(S)*-[M(aet)$_3$] and other metal ions which prefer a tetrahedral coordination geometry. In this paper we describe the preparation and characterization of T-cage-type $Rh^{III}Cd^{II}$ polynuclear complexes composed of *fac(S)*-[Rh(aet)$_3$] units and tetrahedral Cd^{II}. Their properties are discussed in comparison with those of the corresponding T-cage-type $Rh^{III}Zn^{II}$ complexes.

Experimental

Preparation and Resolution of [{Rh(aet)$_3$}$_4$Cd$_3$HO](NO$_3$)$_5$·3H$_2$O (1). To a suspension of *fac(S)*-[Rh(aet)$_3$][13,14] (0.24 g, 0.72 mmol) in 5 cm^3 of water was added a solution of Cd(NO$_3$)$_2$·4H$_2$O (0.56 g, 1.8 mmol) in 1 cm^3 of water. The mixture was stirred at room temperature for 1 h, whereupon the suspension became a clear orange-yellow solution. The reaction solution was stored in a refrigerator for several days and the resulting yellow-orange crystals (**1**) were collected by filtration. One of the yellow-orange crystals was used for X-ray analysis. Yield; 0.18 g (49%). Anal. Calcd for [{Rh(C$_2$H$_6$NS)$_3$}$_4$Cd$_3$HO](NO$_3$)$_5$·3H$_2$O: C, 14.11; H, 3.85; N, 11.65; Rh, 20.14; Cd, 16.50%. Found: C, 13.84; H, 3.76; N, 11.67; Rh, 19.68; Cd, 16.02%.

To a solution of **1** (0.27 g, 0.13 mmol) in 40 cm^3 of water was added a solution of K$_2$[Sb$_2$(*R, R*-tartrate)$_2$]·3H$_2$O (0.13 g, 0.24 mmol) in 55 cm^3 of water. The mixture was allowed to stand at room temperature for two days and the resulting orange-yellow needle crystals, which showed a negative CD value at 400 nm ($(-)^{CD}_{400}$ diastereomer), were collected by filtration. Yield; 0.14 g (59% as a diastereomer). Anal. Calcd for [{Rh(C$_2$H$_6$NS)$_3$}$_4$Cd$_3$HO][Sb$_2$(C$_4$H$_2$O$_6$)$_2$]$_{2.5}$·19H$_2$O: C, 15.12; H, 3.75; N, 4.81; Rh, 11.77; Cd, 9.65%. Found: C, 15.11; H, 3.62; N, 4.79; Rh, 11.85; Cd, 9.81%.

To a suspension of the $(-)^{CD}_{400}$ diastereomer (0.04 g, 0.01 mmol) in 2 cm^3 of water was added a solution of NaNO$_3$ (0.70 g, 8.2 mmol) in 3 cm^3 of water. The mixture was stirred at room temperature for 10 min, followed by standing at room temperature for one week. The resulting yellow-orange crystals were collected by filtration. Yield 0.02 g (85%). Anal. Calcd for [{Rh(C$_2$H$_6$NS)$_3$}$_4$Cd$_3$HO](NO$_3$)$_5$·4H$_2$O·NaNO$_3$: C, 13.43; H, 3.80; N, 11.75%. Found: C, 13.53; H, 3.62; N, 11.57%.

Preparation of [{Rh(aet)$_3$}$_4$Cd$_4$O](NO$_3$)$_6$·5H$_2$O (2). To a suspension of *fac(S)*-[Rh(aet)$_3$][13,14] (0.30 g, 0.91 mmol) in 15 cm^3 of water was added CdO (0.30 g, 2.3 mmol) and Cd(NO$_3$)$_2$·4H$_2$O (0.30 g, 0.97 mmol). The mixture was stirred at room temperature for 1 h, followed by removal of insoluble materials by filtration. The yellow filtrate was allowed to stand at room temperature for one week and the resulting yellow crystals (**2**) were collected by filtration. Yield; 0.27 g (53%). Anal. Calcd for [{Rh(C$_2$H$_6$NS)$_3$}$_4$Cd$_4$O](NO$_3$)$_6$·5H$_2$O: C, 12.79; H, 3.67; N, 11.19; Rh, 18.27; Cd, 19.96%. Found: C, 12.88; H, 3.53; N, 11.16; Rh, 17.82; Cd, 19.58%.

Attempts to optically resolve **2** were unsuccessful; when **2** was treated with K$_2$[Sb$_2$(*R,R*-tartrate)$_2$]·3H$_2$O by the same procedure as that used for **1**, the $(-)^{CD}_{400}$ diastereomer of **1** was isolated.

Measurements. The electronic absorption spectra were recorded with a JASCO Ubest-55 spectrophotometer, and the CD spectra with a JASCO J-600 spectropolarimeter. The concentrations of Rh and Cd in the complexes were determined with a Nippon Jarrel-Ash ICPA-575 ICP spectrophotometer. The ^{13}C NMR spectra were recorded with a Bruker AM-500 NMR spectrometer at the probe temperature in D$_2$O. Sodium 4,4-dimethyl-4-silapentane-1-sulfonate (DSS) was used as the internal reference. The molar conductivities were measured with a Horiba DS-14 conductivity meter at 22 °C in water.

X-Ray Diffraction Study. X-Ray diffraction experiments for **1** were performed on an Enraf

Nonius CAD4 diffractometer with graphite-monochromatized Mo $K\alpha$ radiation (λ=0.71073 Å) at room temperature. Crystal Data: $[\{Rh(aet)_3\}_4Cd_3HO](NO_3)_5\cdot 3H_2O$ = $C_{24}H_{79}N_{17}O_{19}S_{12}Rh_4Cd_3$, M = 2043.7, hexagonal, space group $P6_3mc$ (No. 186), a=15.153(1), c=16.175(1) Å, U= 3216.5(3) Å^3, Z=2, D_c=2.11 g cm^{-3}, D_m=2.13 g cm^{-3}, $F(000)$=2020, μ(Mo $K\alpha$)=22.34 cm^{-1}, and 1413 independent reflections with $F_o > 5\sigma(F_o)$. The structure was solved by direct method and conventional difference Fourier techniques. Rh, Cd, S, N, and O atoms in the complex cation were refined anisotropically, while the other non-H atoms were refined isotropically. H atoms were not included in the calculations. One of five nitrate anions could not be found from the difference maps. The final refinement gave R=0.077 and R_w=0.079 ($w=3.23/\{\sigma^2(F_o)+0.0013(F_o)^2\}$). Atomic positional parameters for the complex cation of **1** are given in Table 1.[15)]

Results and Discussion

The reaction of *fac(S)*-$[Rh(aet)_3]$ with excess $Cd(NO_3)_2$ in water produced yellow-orange crystals (**1**). X-Ray structural analysis of **1** revealed the presence of a pair of enantiomers, which appear to be situated at the same position. One of them is shown in Fig. 1. The entire complex cation of **1** appears to consist of four approximately octahedral *fac(S)*-$[Rh(aet)_3]$ units, four Cd atoms, and one central O atom. However, least-squares refinement of the occupancy factors of Cda and Cdb yielded values of 0.38 and 0.14, respectively, which are approximately three-fourth the values expected for fully-occupied Cda (0.5) and Cdb (0.1667). Moreover, the plasma emission spectral analysis of **1** gave a value of Rh : Cd = 4 : 3.0. These values indicate that **1** actually contains three Cd atoms, which are distributed in four locations with a site occupancy of 3/4 because of the disorder of the complex cation. The molar conductivity of this complex in water is 656 Ω^{-1} cm^2 mol^{-1}, which is in agreement with that of $[\{Rh(aet)_3\}_4Zn_3HO](NO_3)_5$ (641 Ω^{-1} cm^2 mol^{-1}).[12)] From these facts and the elemental analysis, it is reasonable to assign that **1** is a T-cage-type $Rh^{III}{}_4Cd^{II}{}_3$ complex with a "defective" $[Cd_3HO]^{5+}$ core, $[\{Rh^{III}(aet)_3\}_4Cd^{II}{}_3HO](NO_3)_5$, in which the four octahedral *fac(S)*-$[Rh(aet)_3]$ units are bound to the quasi-tetrahedral $[Cd_3HO]^{5+}$ core in a tetrahedral arrangement (Fig. 1). This assignment is supported by its absorption spectral behavior which is quite similar to that of the corresponding T-cage-type $Rh^{III}{}_4Zn^{II}{}_3$ complex, $[\{Rh^{III}(aet)_3\}_4Zn^{II}{}_3HO]^{5+}$ (vide infra).

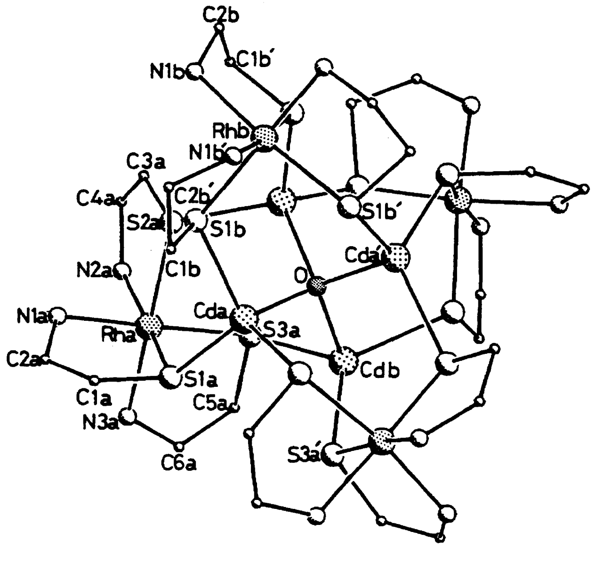

Fig. 1. Perspective view of the complex cation of **1** with the atomic labeling scheme.

The overall structure of the complex cation of **1** resembles that of $[\{Rh(aet)_3\}_4Zn_3HO]^{5+}$.[12)] In particular, the bond distances and angles around the rhodium atoms (average Rh–S = 2.323(12) Å, Rh–N = 2.115(38) Å, S–Rh–S = 95.0(4)°, and N–Rh–N = 90.5(18)°) in **1** are very similar to those found in $[\{Rh(aet)_3\}_4Zn_3HO]^{5+}$ (average Rh–S = 2.329(5) Å, Rh–N = 2.108(18) Å, S–Rh–S = 94.8(2)°, and N–Rh–N = 91.9(8)°). However, the Cd–S (average 2.509(12) Å) and Cd–O (average 2.166(32) Å) distances in **1** are ca. 0.17 Å longer than the Zn–S (average 2.345(6) Å) and Zn–O (average 1.985(20) Å) distances in $[\{Rh(aet)_3\}_4Zn_3HO]^{5+}$, reflecting the difference in covalent radii between the Cd^{II} and Zn^{II} ions. Furthermore, the S–Cd–S (average 115.4(5)°) and S–Cd–O (average 101.9(8)°) angles deviate greatly from the ideal tetrahedral angle of 109.5°, compared with the S–Zn–S (average 112.3(2)°) and S–Zn–O (107.3(5)°) angles in $[\{Rh(aet)_3\}_4Zn_3HO]^{5+}$. Accordingly, it is seen that the formation of **1** is accompanied by significant distortion from the regular tetrahedral geometry for Cd^{II}.

Five isomers ($\Delta\Delta\Delta\Delta$, $\Lambda\Lambda\Lambda\Lambda$, $\Delta\Delta\Delta\Lambda$, $\Lambda\Lambda\Lambda\Delta$, and $\Delta\Delta\Lambda\Lambda$) are possible for **1**, considering the absolute configuration (Δ or Λ) for each of the four *fac(S)*-$[Rh(aet)_3]$ units. However, all the four *fac(S)*-$[Rh(aet)_3]$ units take the same absolute configuration to give only the $\Delta\Delta\Delta\Delta$ and $\Lambda\Lambda\Lambda\Lambda$ isomers (Fig. 1). The selective formation of the $\Delta\Delta\Delta\Delta$ and $\Lambda\Lambda\Lambda\Lambda$ isomers has commonly been recognized for the previous T-cage-type complexes, $[\{Rh(aet)_3\}_4Zn_3HO]^{5+}$ and $[\{M(aet)_3\}_4M'_4O]^{6+}$ (M = Co^{III}, Rh^{III}, or Ir^{III}; $M'_4 = Zn^{II}{}_xCo^{II}{}_{4-x}$), and has been ascribed to the non-bonding interactions of the chelate rings between the Δ- and Λ-*fac*(S)-$[M(aet)_3]$ units in the T-cage-type structure.[9—13)]

As illustrated in Fig. 2, the absorption spectrum of $[\{Rh(aet)_3\}_4Cd_3HO]^{5+}$ (**1**) is quite similar to that of $[\{Rh(aet)_3\}_4Zn_3HO]^{5+}$,[12)] showing two d–d transition bands at 26.3 and 30.3×10^3 cm^{-1} with a shoulder at the lower energy side (ca. 23×10^3 cm^{-1}) and an intense sulfur-to-rhodium charge transfer (CT) band at 44.25×10^3 cm^{-1}. This result obviously implies that the absorption spectra of **1** and $[\{Rh(aet)_3\}_4Zn_3HO]^{5+}$ are dominated by the *fac(S)*-$[Rh(aet)_3]$ units, which adopt quite similar structures in these complexes. In the CD spectrum, the $(-)^{\rm CD}_{400}$ isomer of **1** gives a major neg-

Table 1. Final Atomic Coordinates, Equivalent Isotropic ($B_{eq}/\text{Å}^2$) or Isotropic ($B/\text{Å}^2$) Thermal Parameters, and Occupancy Factors (occ) for the Complex Cation of **1**

Atom	x	y	z	B_{eq}[a)]	occ
Rha	0.3555(2)	0.17774(8)	0.0824(3)	4.63(8)	0.5
S1a	0.4354(9)	0.0915(10)	0.1070(7)	6.7(6)	0.5
S2a	0.4128(8)	0.2798(8)	0.2036(7)	6.2(5)	0.5
S3a	0.4851(8)	0.3080(10)	0.0001(6)	6.2(5)	0.5
N1a	0.237(3)	0.072(3)	0.149(3)	7.6(23)	0.5
N2a	0.269(3)	0.259(3)	0.068(3)	11.8(29)	0.5
N3a	0.295(2)	0.097(3)	−0.033(2)	6.4(19)	0.5
Rhb	0.6667	0.3333	0.4200	4.0(1)	1/6
S1b	0.6530(8)	0.4560(8)	0.3440(8)	5.5(5)	0.5
N1b	0.554(3)	0.331(3)	0.494(2)	8.9(21)	0.5
Cda	0.5907(1)	0.4093(1)	0.1981(3)	7.1(2)	0.375
Cdb	0.6667	0.3333	0.0115(4)	5.6(2)	0.125
O	0.6667	0.3333	0.150(2)	4.2(11)	1/6
				B	
C1a	0.345(3)	−0.019(4)	0.165(4)	11.5(23)	0.5
C2a	0.247(3)	−0.020(4)	0.161(3)	6.7(10)	0.5
C3a	0.335(3)	0.339(3)	0.197(3)	6.7(12)	0.5
C4a	0.268(5)	0.330(5)	0.128(3)	10.3(17)	0.5
C5a	0.433(3)	0.251(3)	−0.101(2)	6.5(10)	0.5
C6a	0.352(4)	0.144(3)	−0.108(3)	9.8(17)	0.5
C1b	0.546(1)	0.454(1)	0.392(2)	7.3(8)	0.5
C2b	0.564(1)	0.436(1)	0.480(2)	9.5(11)	0.5

a) B_{eq} is the arithmetic mean of the principal axes of the thermal ellipsoid.

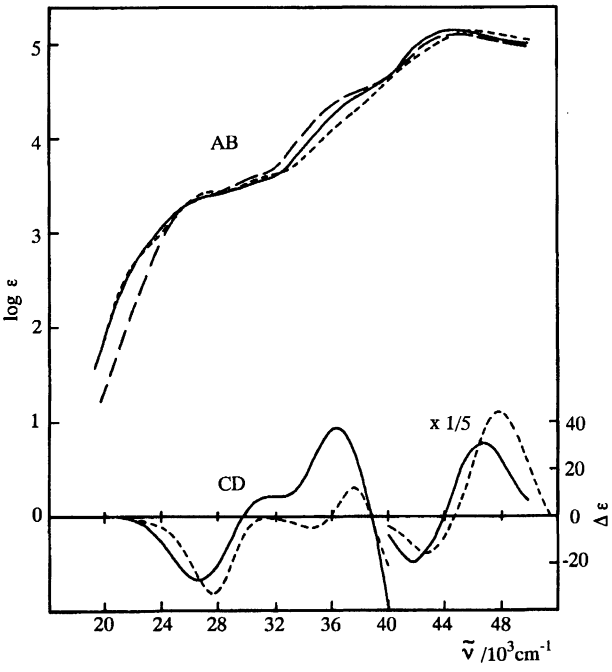

Fig. 2. Visible-UV absorption and CD spectra of $\Delta\Delta\Delta\Delta$-$[\{Rh(aet)_3\}_4Cd_3HO]^{5+}$ ($(-)^{CD}_{400}$-**1**) (—), $\Delta\Delta\Delta\Delta$-$[\{Rh(aet)_3\}_4Zn_3HO]^{5+}$ (---), and $[\{Rh(aet)_3\}_4Cd_4O]^{6+}$ (**2**)(−−). ε values are given in units of mol^{-1} dm^3 cm^{-1}.

ative CD band (26.72×10^3 cm^{-1}) in the d–d absorption band region and a negative and a positive CD bands (41.74×10^3 and 46.77×10^3 cm^{-1}, respectively) in the sulfur-to-rhodium CT band region (Fig. 2). This CD spectral feature coincides well with that of $\Delta\Delta\Delta\Delta$-$[\{Rh(aet)_3\}_4Zn_3HO]^{5+}$,[12] suggesting that $(-)^{CD}_{400}$-**1** has the $\Delta\Delta\Delta\Delta$ configuration.

1 with a "defective" $[Cd_3HO]^{5+}$ core is unstable in water, like $[\{Rh(aet)_3\}_4Zn_3HO]^{5+}$.[12] In the sulfur-to-rhodium CT band region, the CD spectrum of $\Delta\Delta\Delta\Delta$-**1** drastically changes to give one positive CD band at 43.48×10^3 cm^{-1} after 1h, while the CD bands in the d–d region change only slightly. A quite similar CD spectral change has been recognized for $\Delta\Delta\Delta\Delta$-$[\{Rh(aet)_3\}_4Zn_3HO]^{5+}$ in water,[12] although the change for **1** ($K_{obsd}=9.4\times10^4$s^{-1} and $T_{1/2}$=12 min) is three times faster than that for $[\{Rh(aet)_3\}_4Zn_3HO]^{5+}$ ($K_{obsd}=3.2\times10^4$s^{-1} and $T_{1/2}$=36 min).[16] Since the CD spectral change for $[\{Rh(aet)_3\}_4Zn_3HO]^{5+}$ has been ascribed to the cleavage of Zn–S bonds, it is considered that cleavage of Cd–S bonds also occurs in **1**, which is easier than the cleavage of Zn–S bonds in $[\{Rh(aet)_3\}_4Zn_3HO]^{5+}$.

The reaction of *fac(S)*-$[Rh(aet)_3]$ with a mixture of excess $Cd(NO_3)_2$ and CdO in water produced **2**, which contains Rh and Cd in a ratio of 4 : 4. The absorption spectrum of **2** is similar to that of **1** over the whole region (Fig. 2). However, the d–d absorption bands for **2** are clearer than those for **1** and furthermore, no absorption shoulder is observed at the lower energy side of the d–d bands. This absorption spectral behavior coincides well with that of $[\{Rh(aet)_3\}_4Zn_4O]^{6+}$.[13] Considering these facts, molar conductivity (781 $\Omega^{-1}\,\mathrm{cm}^2\,\mathrm{mol}^{-1}$), and elemental analysis, **2** is assignable as the T-cage-type $\mathrm{Rh^{III}}_4\mathrm{Cd^{II}}_4$ complex with a "complete" $[\mathrm{Cd_4O}]^{6+}$ core, $[\{\mathrm{Rh(aet)_3}\}_4\mathrm{Cd_4O}]^{6+}$. In the ^{13}C NMR spectrum, **2** exhibits only two methylene carbon signals for the 12 aet ligands (δ=34.21 and 51.95). The same ^{13}C NMR spectral behavior has been observed for $\Delta\Delta\Delta\Delta/\Lambda\Lambda\Lambda\Lambda$-$[\{\mathrm{Rh(aet)_3}\}_4\mathrm{Zn_4O}]^{6+}$ (δ=33.86 and 51.20),[13] which reflects the T symmetry of the structure. Thus, it is likely that **2** also forms only a pair of enantiomers, $\Delta\Delta\Delta\Delta$ and $\Lambda\Lambda\Lambda\Lambda$. **2** is not stable in water and attempts to optically resolve **2** with the use of $\mathrm{K_2[Sb_2(}R,R\mathrm{\text{-}tartrate)_2]}$ resulted in the formation of optically active **1**. This is in contrast to the fact that $[\{\mathrm{Rh(aet)_3}\}_4\mathrm{Zn_4O}]^{6+}$ is very stable in water and can be formed by standing an aqueous solution of $[\{\mathrm{Rh(aet)_3}\}_4\mathrm{Zn_3HO}]^{5+}$.[13] X-Ray analysis of $[\{\mathrm{Rh(aet)_3}\}_4\mathrm{Zn_4O}]^{6+}$ has shown that the four $\mathrm{Zn^{II}}$ atoms fit well in the T-cage-type structure, having a normal tetrahedral geometry (average S–Zn–S=110.6(1)° and S–Zn–O=108.3(4)°.[13] Taking this fact and the crystal structure of **1** into consideration, it is assumed that in the solid state the four $\mathrm{Cd^{II}}$ atoms are restricted to a highly distorted tetrahedral geometry in the $\mathrm{Rh^{III}}_4\mathrm{Cd^{II}}_4$ T-cage-type structure, which is responsible for the instability of **2** in solution.

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15) Experimental details, lists of atomic coordinates and equivalent isotropic thermal parameters, bond distances and angles, anisotropic thermal parameters, and structure factors for **1** are deposited as Document No. 67039 at the Office of the Editor of the Bull. Chem. Soc. Jpn.

16) The first order rate constant (K_{obsd}) was evaluated according to the treatment described in Ref. 12.