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Preparation and Characterization of $[M^{III}(SeCH_2CH_2NH_2)\{N(CH_2CH_2NH_2)_3\}]^{2+}$ (M^{III} = Co, Rh) and Molecular Structure of the Perchlorate of the Rhodium(III) Complex

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Abstract

By reaction of $[RhCl_2(tren)]^+$ (tren = tris(2-aminoethyl)amine) with $CH_3SeCH_2CH_2NH_2$ in water in the presence of $NaBH_4$, or in its absence in ethanol, only one of the two geometrical isomers of $[Rh(SeCH_2CH_2NH_2)(tren)]^{2+}$ was formed. Both of the two geometrical isomers of the corresponding Co^{III} complex were formed by the reaction of Co^{II}–tren species with $(NH_2CH_2CH_2Se–)_2$. The structure of the Rh^{III} complex was determined by the X-ray method. Crystal data $[Rh(C_2H_6NSe)(C_6H_{18}N_4)](ClO_4)_2$, monoclinic, space group $P2_1/c$, $a = 9.012(1)$, $b = 14.438(1)$, $c = 14.550(4)$ Å, $\beta = 104.81(1)°$, and $Z = 4$. The final R value was 0.026. The complex ion has a distorted octahedral structure with *cis*(tertiary amine nitrogen, Se) configuration. The Rh–N bond length for the amine nitrogen bonded *trans* to the selenium atom is longer by 0.039(6) Å than the average *cis* Rh–N distance for the two other primary amine nitrogens of the tren ligand, indicating *trans* influence of the selenium atom.

Introduction

The interactions between selenol and transition metals are of interest because of the biological roles of selenium [1]. It has been shown that the thiolato sulfur and selenolato selenium in cobalt(III) complexes exert a significant structural *trans* effect [2] and that the effect is related to several of the chemical and kinetic effects induced by coordinated sulfur [3]. Thus, it is of interest to study the chemistry of the selenolato rhodium(III) complex, because both cobalt(III) and rhodium(III) ions have the d^6 configuration.

For the $[M^{III}(SeCH_2CH_2NH_2)(tren)]^{2+}$ (M^{III} = Co, Rh; tren = tris(2-aminoethyl)amine) complex two (*p*- and *t*-) geometrical isomers** are possible, and it is necessary to assign their configurations in order to study their chemistry. This paper describes the preparation of the complexes and X-ray structure analysis of *p*-$[Rh(SeCH_2CH_2NH_2)(tren)]^{2+}$. The spectroscopic properties of the complexes are compared with one another.

Experimental

p-$[Co(SeCH_2CH_2NH_2)(tren)](ClO_4)_2$ *and* *t*-$[Co(SeCH_2NH_2)(tren)]ZnCl_4\cdot 2H_2O$

These complexes were prepared by a method similar to that for the corresponding thiolato complexes [4]. An aqueous solution (60 cm^3) containing tren·3HCl [5] (32.1 g, 0.125 mol) and NaOH (15.1 g, 0.375 mol) was deoxygenated with nitrogen, and then transferred by a syringe into a deoxygenated, aqueous solution (60 cm^3) of $CoCl_2\cdot 6H_2O$ (29.89 g, 0.125 mol) with stirring. To the resulting purple solution was added a deoxygenated, aqueous solution (60 cm^3) containing $(NH_2CH_2CH_2Se\text{-})_2\cdot 2HCl$ [6] (24.1 g, 0.075 mol) and NaOH (6.03 g, 0.151 mol). The mixture was allowed to stand in a nitrogen atmosphere for 5 days at room temperature. A small portion of the resulting brown solution was set aside for examination of the formation ratio

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**The Se atoms in the *p*- and *t*-isomers are *trans* to the primary (p) and tertiary (t) tren amine nitrogens, respectively.

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of the isomers, and to the majority was added 20 cm^3 of 70% $HClO_4$. The brown crystals which precipitated were collected by filtration, washed with ethanol, and air-dried. The complex was the *p*-isomer (*vide infra*). The mother liquor was diluted with water, and applied on a column (ϕ 7 cm × 30 cm) of SP-Sephadex C-25. By elution with 0.15 mol dm^{-3} Na_2SO_4, two bands appeared; a faster-moving brown band (*p*-isomer) and a slower-moving dark brown band (*t*-isomer). The eluate containing the *p*-isomer was diluted with water and applied on a column of SP-Sephadex C-25. After washing the column with water, the complex was eluted with 1 mol dm^{-3} $NaClO_4$. Upon evaporation of the eluate to a small volume and cooling, the perchlorate of the *p*-isomer was obtained. The total yield of the *p*-isomer was 37.9 g. *Anal.* Found: C, 18.38; H, 4.66; N, 13.55%. Calcd. for $C_8H_{24}N_5Cl_2CoO_8Se$: C, 18.23; H, 4.60; N, 13.30%.

The eluate containing the *t*-isomer was applied on a column of Dowex 50W-X2 (H$^+$ form, 200–400 mesh), and the adsorbed complex was eluted with 2 mol dm^{-3} HCl. The dark brown eluate was evaporated to a small volume, and to the concentrate was added an excess of $ZnCl_2$ in 3 mol dm^{-3} HCl to yield dark brown crystals of the tetrachlorozincate of the *t*-isomer. Yield: 13.5 g. *Anal.* Found: C, 17.07; H, 4.82; N, 12.24%. Calcd. for $C_8H_{28}N_5O_2SeCl_4CoZn$: C, 16.82; H, 4.94; N, 12.26%.

The perchlorate of the *t*-isomer was obtained by the addition of $HClO_4$ to an aqueous solution of the tetrachlorozincate.

The formation ratio of the *p*- to *t*-isomer contained in the reaction mixture was found by column chromatography to be 3:1 (SP-Sephadex C-25, 0.15 mol dm^{-3} Na_2SO_4).

p-[Rh(SeCH$_2$CH$_2$NH$_2$)(tren)](ClO$_4$)$_2$

To a hot (70–80 °C) aqueous solution (75 cm^3) containing $[RhCl_2(tren)]Cl$ [7] (0.50 g, 1.41 mmol), $CH_3SeCH_2CH_2NH_2 \cdot HCl$ [8] (0.30 g, 1.72 mmol), and NaOH (0.10 g, 2.5 mmol) was added a speck of $NaBH_4$, the color of the solution changing from yellow to orange. After stirring for 15 min at *ca.* 80 °C, the reaction mixture was cooled to room temperature, and applied on a column (ϕ 1.2 cm × 25 cm) of SE-Toyopearl HW-40 (fine)*. The product was eluted with 0.15 mol dm^{-3} Na_2SO_4 and the eluate of the first yellow band was collected, a brown band remaining at the top of the column. The eluate was diluted with water and applied again on a column (ϕ 1.2 × 2 cm) of SE-Toyopearl HW-40 (fine). The column was washed with water, and the complex eluted with 1 mol dm^{-3} $NaClO_4$. The eluate was concentrated to a small volume in a desiccator over P_2O_5 to yield orange crystals, which were collected by filtration, washed with ethanol, and air-dried. Yield: 0.22 g. *Anal.* Found: C, 16.78; H, 4.36; N, 12.28%. Calcd. for $C_8H_{24}N_5Cl_2O_8RhSe$: C, 16.83; H, 4.24; N, 12.26%.

Demethylation occurred in the course of the preparation, as confirmed by the ^{1}H NMR spectrum and the X-ray analysis.

The complex was also prepared with ethanol as a solvent without the addition of $NaBH_4$. A solution of $[RhCl_2(tren)]Cl$ (0.10 g, 0.281 mmol), $CH_3SeCH_2CH_2NH_2 \cdot HCl$ (0.050 g, 0.287 mmol), and NaOH (0.024 g, 0.60 mmol) in ethanol (20 cm^3) was refluxed for 1 h. The reaction mixture was diluted with water, and chromatographed as described above. Yield: 0.020 g.

Measurements

UV–Visible and ^{1}H NMR spectra were measured with a Hitachi 323 spectrophotometer and a JEOL PMX-60 spectrometer, respectively. Infrared spectra were recorded on a JASCO A-3 spectrophotometer using potassium bromide plates.

Crystal Structure Determination

The crystal specimen used was orange in color and of a prismatic shape with dimensions 0.3 × 0.3 × 0.4 mm^3. The cell dimensions were refined based on 20 2θ values ($36 < 2\theta < 43°$) with (MoKα_1) = 0.70926 Å. The crystal data are: $[Rh(C_2H_6NSe)(C_6H_{18}N_4)](ClO_4)_2$, F.W. 571.1; monoclinic, space group $P2_1/c$, $a = 9.012(1)$, $b = 14.438(1)$, $c = 14.550(4)$ Å and $\beta = 104.81(1)°$, $V = 1830.3(6)$ Å^3, $Z = 4$, $D_x = 2.07$ Mg m^{-3}, $\mu = 3.23$ mm^{-1}. Intensities were measured using graphite monochromatized MoKα radiation on an automated Rigaku four-circle diffractometer AFC-5. The ω–2θ scan technique was employed at a scan rate of 2° min^{-1} in ω. 2733 reflections were measured up to $2\theta = 55°$, of which 2622 reflections with $|F_o| > 3\sigma$ were regarded as observed. The usual corrections were made for Lorentz and polarization factors, and for absorption. The structure was solved by the heavy atom method. Positions of the Rh and Se atoms were deduced from the prominent peaks in the Patterson function. Other non-H atoms were located by application of Fourier syntheses and refined with anisotropic thermal parameters. All the H atoms were found from the difference synthesis and refined with isotropic thermal parameters. The atomic parameters were refined by block-diagonal least squares. The function minimized was $\Sigma w \| F_o | - | F_c \|^2$, $w^{-1} = \sigma^2(|F_o|) + (0.015|F_o|)^2$. All the

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*Toyopearl, the product of Toyo Soda Mfg. Co., Ltd. (Tokyo, Japan) is the same material as Fractogel TSK available from E. Merck (Darmstadt, F.R.G.).

TABLE I. Positional Parameters ($\times 10^4$, $\times 10^5$ for Rh and Se) and Equivalent Isotropic Thermal Parameters of non-H Atoms.

	x	y	z	B_{eq} (Å^2)
Rh	48810(3)	10143(2)	27536(2)	2.0
Se	60715(5)	−3735(3)	36009(4)	2.8
Cl(1)	1438(1)	3624(1)	3522(1)	3.3
Cl(2)	7341(1)	2481(1)	5853(1)	3.6
O(1)1	1349(6)	4590(3)	3600(4)	8.4
O(1)2	3009(4)	3345(3)	3865(3)	5.9
O(1)3	543(6)	3178(4)	4014(4)	8.6
O(1)4	944(7)	3370(4)	2546(4)	9.5
O(2)1	6012(7)	2782(3)	5186(4)	10.5
O(2)2	8190(6)	3265(3)	6217(4)	8.6
O(2)3	8152(8)	1838(4)	5485(4)	11.9
O(2)4	6896(6)	2067(3)	6637(4)	7.1
N(1)	2742(4)	478(2)	2192(3)	2.5
N(2)	5349(4)	466(2)	1536(3)	3.1
N(3)	3865(4)	2231(2)	2057(3)	3.3
N(4)	4073(4)	1313(2)	3934(3)	2.7
N(5)	7043(4)	1614(2)	3283(3)	2.8
C(1)	2971(5)	−336(3)	1608(4)	3.2
C(2)	3985(6)	−60(3)	975(4)	3.5
C(3)	1707(5)	1191(3)	1587(4)	3.6
C(4)	2568(6)	1967(3)	1278(4)	3.9
C(5)	2156(5)	222(3)	3022(4)	3.3
C(6)	2443(5)	1013(3)	3728(3)	3.1
C(7)	8331(5)	959(3)	3419(4)	3.4
C(8)	8144(5)	152(3)	4014(4)	3.8

shifts in the final cycle of the refinement were less than 0.5σ for non-H atoms. The final R was 0.026 and wR = 0.035 for the 2622 observed unique reflections. The calculations were carried out on a FACOM M-180 computer at Keio University, with the Universal Crystallographic Computation Program System UNICS III [10]. Final atomic parameters of non-H atoms are listed in Table I.

Results and Discussion

The *p*- and *t*-isomers of $[Co(SeCH_2CH_2NH_2)(tren)]^{2+}$ were prepared by oxidizing Co^{II}–tren species with the diselenide, $(NH_2CH_2CH_2Se\text{-})_2$ analogous to the method of preparation for the corresponding thiolato complexes [4]. The isomers can be assigned on the basis of the elution order in column chromatography. The *p*-isomer has two pairs of three facially arranged NH_2 groups, capable of forming hydrogen bonds with a sulfate ion thereby forming a stronger ion-pair than the *t*-isomer, which lacks this symmetry. Thus the *p*-isomer should be eluted faster than the *t*-isomer [11]. The corresponding thiolato complexes, which were assigned on the basis of the absorption spectra, reactivity, etc. [4], show the same elution order. The characteristics of the absorption spectra of the isomers thus assigned resemble those of the corresponding isomers of the thiolato complexes [4]. The *t*-isomer of the selenolato complex shows a maximum at *ca.* 16000 cm^{-1}, whereas the *p*-isomer only a weak shoulder in this region (Fig. 1 and Table II). The complexes, $[Co(XCH_2CH_2NH_2)(en)_2]^{2+}$ (X = S, Se; en = ethylenediamine) also show a band at *ca.* 16000–17000 cm^{-1}, and this absorption was assigned by Houlding *et al.* [12] to one of the spin-allowed d–d transition components. The first absorption band (*ca.* 20500 cm^{-1}) of $[Co(SeCH_2CH_2NH_2)(tren)]^{2+}$ is at lower energy than that of the corresponding thiolato complex, and the second absorption band of the former complex is not observed because of

TABLE II. Absorption Spectral Data.

Complex	$\tilde{\nu}_{max}$/cm^{-1}	log ϵ
p-$[Co(SeCH_2CH_2NH_2)(tren)]^{2+}$	16700[a]	1.64
	20400	2.30
	32700	4.17
	47600	4.10
t-$[Co(SeCH_2CH_2NH_2)(tren)]^{2+}$	16100	1.79
	20800	2.21
	32600	4.26
	49000	4.19
p-$[Rh(SeCH_2CH_2NH_2)(tren)]^{2+}$	25000[a]	1.86
	32500	2.94
	41000	4.35

[a] Shoulder.

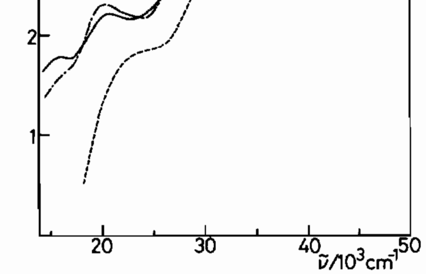

Fig. 1. Absorption spectra of the *t*-(——) and *p*-(–·–) isomers of $[Co(SeCH_2CH_2NH_2)(tren)]^{2+}$, and of *p*-$[Rh(SeCH_2CH_2NH_2)(tren)]^{2+}$ (------).

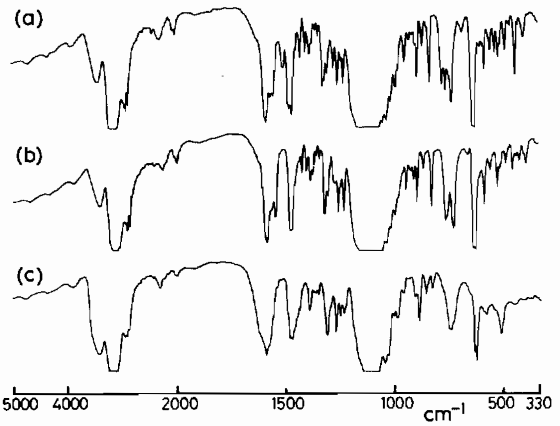

Fig. 2. Infrared spectra of [Rh(SeCH$_2$CH$_2$NH$_2$)(tren)]-(ClO$_4$)$_2$ (a) and the *p*-(b) and *t*-(c) isomers of [Co(SeCH$_2$-CH$_2$NH$_2$)(tren)](ClO$_4$)$_2$.

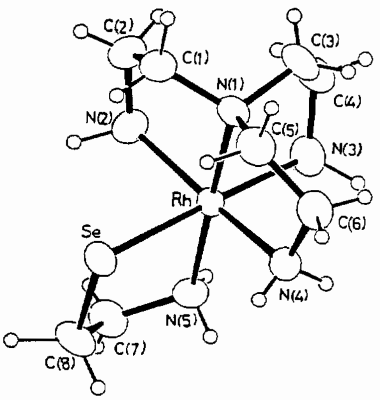

Fig. 3. An ORTEP drawing of the complex cation, with thermal ellipsoids scaled at the 50% probability level [15]. H atoms are represented by circles of radius 0.08 Å.

overlapping with a strong Se-to-Co^{III} charge–transfer band.

The rhodium(III) complex, *p*-[Rh(SeCH$_2$CH$_2$-NH$_2$)(tren)]$^{2+}$ was prepared from [RhCl$_2$(tren)]$^+$ and CH$_3$SeCH$_2$CH$_2$NH$_2$ in water in the presence of NaBH$_4$, or in its absence in ethanol, suggesting that the reaction proceeds via Rh^{III}–hydride or Rh^I species. Se-Demethylation was suggested by the elemental analysis and by the ^{1}H NMR spectrum, and was confirmed by the X-ray analysis (*vide infra*). It has been shown that S-dealkylation is promoted by coordination of the aromatic sulfide to metal ions such as Ni^{II}, Pd^{II}, and Au^{III} [13], although aliphatic sulfide–metal complexes are relatively stable toward dealkylation. Se-dealkylation is rare and to our knowledge no other example of S- or Se-dealkylation by formation of a Rh^{III} complex has been reported.

The rhodium(III) complex forms only one geometrical isomer as indicated by column chromatography. The absorption spectrum is shown in Fig. 1, and the numerical data in Table II. The spectrum provides no decisive evidence on the configuration of the isomer. A shoulder absorption at *ca.* 25000 cm^{-1} seems to correspond to the lowest energy component of the cobalt(III) complex, since these bands disappear upon alkylation at the selenium atom [14].

In Fig. 2 the IR spectrum of the rhodium(III) complex is compared with those of the cobalt(III) complexes. The spectral pattern of the rhodium(III) complex is much more similar to that of the *p*-isomer of the cobalt(III) complex than to that of the *t*-isomer. This assignment is confirmed by the X-ray structure determination.

A perspective drawing of the cation of the rhodium(III) complex is presented in Fig. 3. Selected bond distances and angles are listed in Table III. The rhodium atom is octahedrally coordinated by the four nitrogen atoms of tren and the selenium and nitrogen atoms of SeCH$_2$CH$_2$NH$_2$. The complex is the *p*-isomer, in agreement with the assignment based on the IR spectrum. The five-membered chelate ring formed by SeCH$_2$CH$_2$NH$_2$ adopts an envelope conformation. C(7) and C(8) atoms are

TABLE III. Selected Bond Lengths (Å) and Bond Angles (°) and their Estimated Standard Deviations.

Rh–Se	2.451(1)	Rh–N(1)	2.044(3)	Rh–N(2)	2.080(4)
Rh–N(3)	2.116(3)	Rh–N(4)	2.075(5)	Rh–N(5)	2.091(3)
Se–C(8)	1.963(4)				

Se–Rh–N(1)	97.9(1)	N(1)–Rh–N(5)	177.3(1)
Se–Rh–N(2)	87.7(1)	N(2)–Rh–N(3)	93.7(1)
Se–Rh–N(3)	178.5(1)	N(2)–Rh–N(4)	167.1(2)
Se–Rh–N(4)	87.4(1)	N(2)–Rh–N(5)	95.7(2)
Se–Rh–N(5)	84.6(1)	N(3)–Rh–N(4)	91.3(2)
N(1)–Rh–N(2)	83.8(2)	N(3)–Rh–N(5)	94.6(1)
N(1)–Rh–N(3)	82.8(1)	N(4)–Rh–N(5)	95.7(2)
N(1)–Rh–N(4)	85.1(2)	Rh–Se–C(8)	95.6(1)

situated on the same side of the plane formed by Rh, Se, and N(5) atoms by a distance of 0.68 and 0.15 Å, respectively. The Rh–N(1) bond distance of 2.044(3) Å is significantly shorter than those (2.075(5)–2.116(3) Å) for the primary N atoms of tren. This trend was also recognized in the cobalt(III) complexes *p*- and *t*-[Co(glycinate)(tren)]$^{2+}$ [16]. The bond distance Rh–N(3) for nitrogen, bonded *trans* to the selenium atom, is longer by 0.039(6) Å than the average distance of *cis* Rh–N(2) and Rh–N(4) indicating *trans* influence of the selenium atom. This elongation is smaller than that of 0.063(9) Å observed for [Co(SeCH$_2$CH$_2$NH$_2$)(en)$_2$]$^{2+}$ [2a]. The average bond distance between Rh and the N atoms of tren is 2.079(4) Å and longer by 0.12 Å than that of Co–N in [Co{CH$_3$SCH(CH$_3$)COO}(tren)](ClO$_4$)$_2$, so that the mean N–Rh–N in the chelate rings of tren, 84.0(2)°, is slightly smaller than the chelate angle of 86.7(2)° observed in the cobalt(III)–tren complex [17]. The crystal structure consists of discrete molecules separated by normal van der Waals distances.

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Supplementary Material Available

Tables of the anisotropic parameters of the non-H atoms, the coordinates of H atoms, and observed and calculated structure factors are available from Y. Saito on request.

References

1 T. C. Stadtman, *Science, 183,* 915 (1974).

2 (a) R. C. Elder, L. R. Florian, R. E. Lake and A. M. Yacynych, *Inorg. Chem., 12,* 2690 (1973);
(b) C. A. Stein, P. E. Ellis, Jr., R. C. Elder and E. Deutsch, *Inorg. Chem., 15,* 1618 (1976);
(c) M. H. Dickman, R. J. Doedens and E. Deutsch, *Inorg. Chem., 19,* 945 (1980);
(d) K. Okamoto, K. Wakayama, H. Einaga, M. Ohmasa and J. Hidaka, *Bull. Chem. Soc. Jpn., 55,* 3473 (1982).

3 R. C. Elder, M. J. Heeg, M. D. Payne, M. Trkula and E. Deutsch, *Inorg. Chem., 17,* 431 (1978) and references therein.

4 W. G. Jackson and A. M. Sargeson, *Inorg. Chem., 17,* 2165 (1978).

5 H. B. Jonassen and G. T. Strickland, *J. Am. Chem. Soc., 80,* 312 (1958).

6 D. L. Klayman, *J. Org. Chem., 30,* 2454 (1965).

7 S. A. Johnson and F. Basolo, *Inorg. Chem., 1,* 925 (1962).

8 H. Tanaka, H. Sakurai and A. Yokoyama, *Chem. Pharm. Bull., 18,* 1015 (1970).

9 M. Fujita, Y. Yoshikawa and H. Yamatera, *Chem. Lett.,* 437 (1982).

10 T. Sakurai and K. Kobayashi, *Rikagaku Kenkyusho Hokoku, 55,* 69 (1979).

11 K. Sakakibara, Y. Yoshikawa and H. Yamatera, *Bull. Chem. Soc. Jpn., 52,* 2725 (1979).

12 V. H. Houlding, M. Mäcke and A. W. Adamson, *Inorg. Chem., 20,* 4279 (1981).

13 S. G. Murray and F. R. Hartley, *Chem. Rev., 81,* 365 (1981).

14 K. Nakajima, K. Tozaki, M. Kojima and J. Fujita, manuscript in preparation.

15 C. K. Johnson, 'ORTEP', Report ORNL-3794, Oak Ridge National Laboratory, Tenn., 1965.

16 Y. Mitsui, J. Watanabe, H. Harada, T. Sakamaki, Y. Iitaka, Y. Kushi and E. Kimura, *J. Chem. Soc., Dalton Trans.,* 2095 (1976).

17 S. Ohba and Y. Saito, *Acta Crystallogr., Sect. C:, 40,* 398 (1984).