Cationic Rhodium(I) Complexes of 1,4,8,11-Tetrathiacyclotetradecane ([14]aneS_4) and the 6,6,13,13-Tetramethyl Analogue (Me_4[14]aneS_4). Preparation of Two Conformers, *X*-Ray Crystal Structure of {Rh[14]aneS_4}$_2$$Cl_2$·MeCN, and Conformational Effect on the Nucleophilicity of the Rhodium(I) Ion

Toshikatsu Yoshida,[a]* Tatsuo Ueda,[a] Tomohiro Adachi,[a] Kazuhiko Yamamoto,[b] and Taiichi Higuchi[c]*

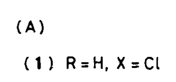
[a] *Department of Chemistry, Faculty of Integrated Arts and Sciences, University of Osaka Prefecture, Sakai, Osaka 591, Japan*

[b] *Laboratory of Organic Chemistry, Osaka Women's University, Sakai, Osaka 590, Japan*

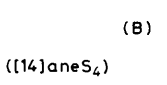
[c] *Department of Chemistry, Faculty of Science, Osaka City University, Sumiyoshiku, Osaka 588, Japan*

Two conformers for the cationic rhodium(I) complexes of the title 14-membered cyclic tetrasulphides have been prepared and the conformational effect upon the nucleophilicity of rhodium(I) ion is shown by the oxidative addition reaction of CH_2Cl_2; {Rh[14]aneS_4}Cl (**1**), in which the Rh atom lies 0.133(2) Å above the plane of four S atoms, forms a dimer through a Rh · · · Rh [3.313(1) Å] and four Rh · · · S [3.697(9)—3.822(3) Å] intermolecular non-bonded interactions as established by an *X*-ray crystal structure determination.

Although the chemical and physical properties of the transition metal complexes of macrocyclic tetrasulphides are markedly affected by the ring size,[1] little is known about the conformational effect of the macrocycles, probably owing to the difficulty in obtaining more than one conformer for macrocycle complexes of the same ring size. Among five possible conformers for square-planar or tetragonal complexes of 1,4,8,11-tetrathiacyclotetradecane ([14]aneS_4), only the up–up–down–down conformer (A) has been established by *X*-ray studies of {Ni[14]aneS_4}$(BF_4)_2$[2] and {Cu[14]aneS_4}-$(ClO_4)_2$.[3] The remaining four conformers are unknown except that the above nickel(II) complex has been proposed to be present as an equilibrium between (A) and the all-up conformer (B) in $MeNO_2$.[4] Here we describe the preparation of two conformers, (A) and (B), for the square-planar complexes [RhL]X {(**1**), L = [14]aneS_4, X = Cl; (**2**), L = Me_4[14]aneS_4, X = Cl; (**3**), L = Me_4[14]aneS_4, X = BPh_4} together with the molecular structure of (**1**). These rhodium(I) complexes were found to be strong nucleophiles and the σ-basicity of the rhodium(I) ion was affected by the conformation of macrocycle.



(A)



(B)

(**1**) R = H, X = Cl ([14]aneS_4)
(**2**) R = Me, X = Cl (Me_4[14]aneS_4)
(**3**) R = Me, X = BPh_4 (Me_4[14]aneS_4)

M = Rh

The reaction of $[RhCl(C_8H_{14})_2]_2$ with [14]aneS_4 (2 mol. equiv.) in toluene at room temperature gave (**1**) as reddish brown crystals (75%).†‡ Prolonged heating (55—60 °C, 70 h) of a mixture of [14]aneS_4 and $[RhCl(cod)]_2$ (cod = cyclo-octa-1,5-diene) in toluene also afforded (**1**) (55%). This contrasts with the formation of {$Rh_2(cod)_2$[20]aneS_6}$(PF_6)_2$ from a similar reaction of 1,4,7,11,14,17-hexathiacycloicosane.[5] The compound (**2**) was prepared similarly from $[RhCl(C_8H_{14})_2]_2$

---

† Satisfactory elemental analyses were obtained.

‡ Compound (**1**) differs in colour from the bright golden compounds {Rh[14]aneS_4}X (X = ClO_4, Br, *etc.*) prepared by reduction of *cis*-{$RhCl_2$[14]aneS_4}$^+$ with $NaBH_4$ (W. D. Lemke, K. E. Travis, N. E. Takvoryan, and D. H. Busch, *Adv. Chem. Ser.*, 1976, **150**, 358). The conformation of the bright golden compound was not elucidated.

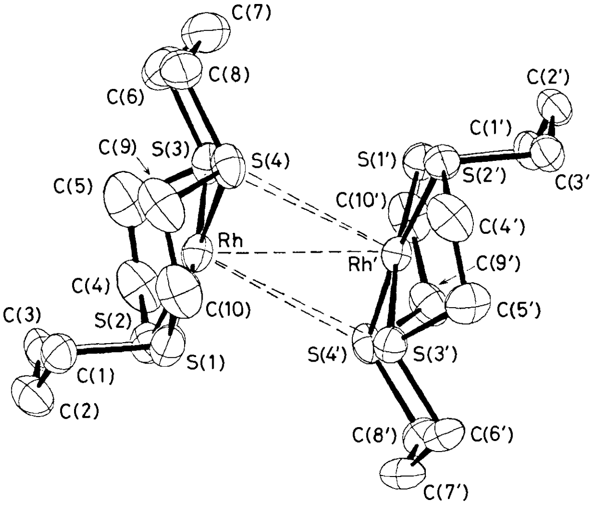


Figure 1. ORTEP drawing (50% probability ellipsoids) showing the dimeric structure of the cation $\{Rh[14]aneS_4\}^+$ (**1**). Principal distances and angles (e.s.d.s. in parentheses): Rh–S(1) 2.285(4), Rh–S(2) 2.282(5), Rh–S(3) 2.261(3), Rh–S(4) 2.264(6) Å; S(1)–Rh–S(2) 87.3(1), S(2)–Rh–S(3) 88.1(1), S(3)–Rh–S(4) 95.8(1), S(4)–Rh–S(1) 87.9(1)°.

and $Me_4[14]aneS_4$ as reddish brown crystals (83%).† The all-up conformation (B) for (**1**) and (**2**) was deduced from their 400 MHz ^1H n.m.r. spectra, which indicate the $\overline{RhSCH_2CR_2CH_2S}$ [R = H for (**1**), Me for (**2**)] and $\overline{RhSCH_2CH_2S}$ rings assume the chair and envelope forms, respectively.§ Isomerization from conformer (B) to (A) took place readily when the reddish brown complex (**2**) was treated with $NaBPh_4$ in MeOH at room temperature, (**3**) being obtained as bright yellow crystals (94%).†§ Both conformations of (**2**) and (**3**), however, are stable in Me_2SO, at least below 100 °C. The all-up conformation of (**1**) was confirmed by an *X*-ray structural study (Figure 1).

Crystal data:¶ $C_{20}H_{40}Cl_2Rh_2S_8{\cdot}MeCN$ (grown from MeCN), M = 854.8, monoclinic, space group $P2_1/c$, a = 11.520(1), b = 18.160(1), c = 18.115(1) Å, β = 116.92(4)°, U = 3379.1(3) Å^3, Z = 4, D_c = 1.680 g cm^{-3}, $\mu(\text{Mo-}K_\alpha)$ = 9.68 cm^{-1}, λ = 0.7107 Å. 5993 Independent reflections ($4<2\theta<55°$) were measured on a Philips PW1100 diffractometer. The structure was solved by direct methods and refined by block-diagonal least-squares for the 3371 reflections with $I>3\sigma(I)$. The positions of the H atoms were located in the difference Fourier synthesis and were refined isotropically. The final R and R_w values are 0.040 and 0.060, respectively. The geometry around the Rh atom is slightly distorted square planar, the Rh atom being 0.133(2) Å above the plane of four S atoms which are strictly coplanar [deviations <0.002(3) Å]. The Rh–S bond distances [2.261(3)—2.285(4) Å] are significantly shorter than those (2.29—2.50 Å) found in rhodium(I) thiolato and sulphide complexes.[5—7] Compound (**1**) is a dimer composed of two crystallographically independent monomers joined through a Rh · · · Rh [3.313(1) Å] and four Rh · · · S [3.697(9)—3.822(3) Å] intermolecular non-bonded interactions. Thus, the dimer has approximately C_{2h} symmetry. The Rh · · · Rh separation is comparable to that observed in $[RhCl(CO)_2]_2$ (3.31 Å).[8] The Rh · · · S interactions, albeit weak, are reflected in the difference of the angles between the S(4)–C(8) and S(1)–C(1) vectors and the plane of four S atoms; the angle involving the S(4) atom [42(1)°] is 24° less than the corresponding angle of the free S(1) atom, indicating that the S(4)–C(8) bond bends so as to give the maximum Rh · · · S non-bonded interaction.

The rhodium(I) complexes (**1**), (**2**), and (**3**) were found to be strong nucleophiles. Thus, oxidative addition of CH_2Cl_2 occurred readily at room temperature affording *trans*-$[RhCl(CH_2Cl)L]X$ {L = $[14]aneS_4$, X = Cl; L = $Me_4[14]aneS_4$, X = Cl; or L = $Me_4[14]aneS_4$, X = BPh_4},† which give $RhCH_2Cl$ ^1H signals at δ 4.32 (d, $J_{Rh\text{-}H}$ 2.8 Hz), 4.21 (d, $J_{Rh\text{-}H}$ 2.8 Hz), and 4.26 (d, $J_{Rh\text{-}H}$ 2.9 Hz), respectively. The high nucleophilicity of the 14-membered cyclic tetrasulphide complexes, which contrasts with the inertness of $RhCl(PPh_3)_3$ and $[Rh(CNBu^t)]_4^+$ towards CH_2Cl_2, is probably due to the low π-acidity of sulphide ligands.[9] In addition, the conformation of the macrocyclic ligand was found to affect the σ-basicity of the rhodium(I) ion. The rate of oxidative addition of CH_2Cl_2 to (**2**) was 7 times faster than that to (**3**), the second-order rate constants being 7.4×10^{-3} and 1.1×10^{-3} dm^3 mol^{-1} min^{-1} [$(CD_3)_2SO$, 25 °C], respectively. The high nucleophilicity of (**2**) may be attributable to the deviation of the Rh atom from the plane of four S atoms since the Rh atom in the up–up–down–down conformer of (**3**) is expected to be exactly in the plane.

This work was supported partly by the Joint Studies Program of the Institute for Molecular Sciences and by a Grant-in-Aid for Scientific Research from the Ministry of Education, Japan, T. A. and T. H. are indebted to the Crystallographic Research Center, Institute for Protein Research, and Computation Center, Osaka University for computer calculations.

Received, 24th May 1985; Com. 714

---

§ The envelope form of the $\overline{RhSCH_2CH_2S}$ ring in (**1**) and (**2**) and the half-chair form in (**3**) were assigned by simulating the ^1H n.m.r. spectra of the SCH_2CH_2S protons employing the following parameters (*J* values in Hz): 400 MHz ^1H n.m.r.: (**1**) (CD_3OD): δ−0.21 (dtt, J_{gem} −16.1, J_{vic} 1.8, 11.7, $SCH_2CH_2CH_2S$), 0.58 (dtt, J_{gem} −16.1, J_{vic} 1.7, 5.9, $SCH_2CH_2CH_2S$), 0.94 (ddd, J_{gem} −11.7, J_{vic} 1.7, 11.7, $SCH_2CH_2CH_2S$), 1.25 (ddd, J_{gem} −11.7, J_{vic} 1.8, 5.9, $SCH_2CH_2CH_2S$), and 0.91 and 1.01 (m, J_{gem} −12.34, J_{vic} 4.75, 8.00, SCH_2CH_2S); (**2**) [$(CD_3)_2SO$]: δ 1.05 and 1.17 (s, Me), 2.98 and 3.05 (d, J_{gem} 11.2, $SCH_2CMe_2CH_2S$), and 2.90 and 3.01 (m, J_{gem} −12.07, J_{vic} 4.32, 9.13, SCH_2CH_2S); (**3**) [$(CD_3)_2SO$]: δ 1.11 and 1.22 (s, Me), 2.82 and 3.01 (d, J_{gem} 11.0, $SCH_2CMe_2CH_2S$), 2.84 and 3.01 (m, J_{gem} −10.34, J_{vic} 10.50, 2.58, 2.00, SCH_2CH_2S).

¶ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

References

1 U. B. Pett, L. L. Diaddario, E. R. Dokal, P. W. Corfield, C. Ceccarelli, M. D. Glick, L. A. Ochrymowycz, and D. B. Rorabacher, *Inorg. Chem.*, 1983, **22**, 3661, and references cited therein.
2 P. H. Davis, L. K. White, and R. L. Belford, *Inorg. Chem.*, 1975, **14**, 1753.
3 M. D. Glick, D. P. Gavel, L. L. Diaddario, and D. B. Rorabacher, *Inorg. Chem.*, 1976, **15**, 1190.
4 N. Herron, O. W. Howarth, and P. Moore, *Inorg. Chim. Acta*, 1976, **20**, L43.
5 D. P. Riley and J. D. Oliver, *Inorg. Chem.*, 1983, **22**, 3361.
6 A. Tiripicchio, M. Tiripicchio Camellini, C. Claver, A. Ruiz, and L. A. Oro, *J. Organomet. Chem.*, 1983, **241**, 77.
7 D. G. VanDerveer and R. Eisenberg, *J. Am. Chem. Soc.*, 1974, **96**, 4997.
8 L. F. Dahl, C. Martell, and D. L. Wampler, *J. Am. Chem. Soc.*, 1961, **83**, 1761.
9 S. G. Murray and F. R. Hartley, *Chem. Rev.*, 1981, **81**, 365.