Ring Size Effect of Crown Thioethers upon Recognition of Hydrido and Chloro Ligands at Stereochemically Different Axial Sites in *trans*-RuH(Cl)L (L = *syn*-Me_4[14]aneS_4, *syn*-Me_8[16]aneS_4)†

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Hydrido and chloro ligands in *trans*-RuH(Cl)(*syn*-Me_4[14]aneS_4) co-ordinate selectively at the stereochemically congested and uncongested axial sites, respectively, while the corresponding 16-membered analogue *trans*-RuH(Cl)(*syn*-Me_8[16]aneS_4) exists as a mixture of two geometrical isomers; the crystal structure of the former is reported.

Ring size is a fundamental parameter of polydentate crown thioethers determining the stereochemistry of their metal complexes. For example, a quadridentate 16-membered crown thioether has been shown to give seven co-ordinate Hg[16]aneS_4(ClO_4)$_2$ where one of the ClO_4^- ions is attached as a bidentate ligand,[1] while the corresponding 14-membered macrocycle afforded a square pyramidal complex {Hg[14]aneS_4(H_2O)}$^{2+}$.[2] Here we report a novel ring size effect controlling stereospecific co-ordination of the axial hydrido and chloro ligands in *trans*-RuH(Cl)L {(**1**) L = *syn*-Me_4[14]aneS_4; (**2**) L = *syn*-Me_8[16]aneS_4}.†

Reaction of *cis*-Ru$Cl_2$$Me_4$[14]ane$S_4$[3] with a large excess of NaBH_4 in MeOH at ambient temperature gave (**1**) as bright yellow crystals (72%) (Scheme 1).‡ The co-ordinated Me_4[14]aneS_4 adopts a *syn* conformation with alternative chair and envelope forms for the $\overline{\mathrm{RuSCH_2CMe_2CH_2S}}$ and $\overline{\mathrm{RuSCH_2CH_2S}}$ rings, respectively. In the *syn* conformer the two axial co-ordination sites are in stereochemically different environments; the site surrounded by the macrocyclic C atoms is congested, while the opposite site is uncluttered. Owing to the axial asymmetry of (**1**), two geometrical isomers are possible. The observation of a single ν(Ru–H) band

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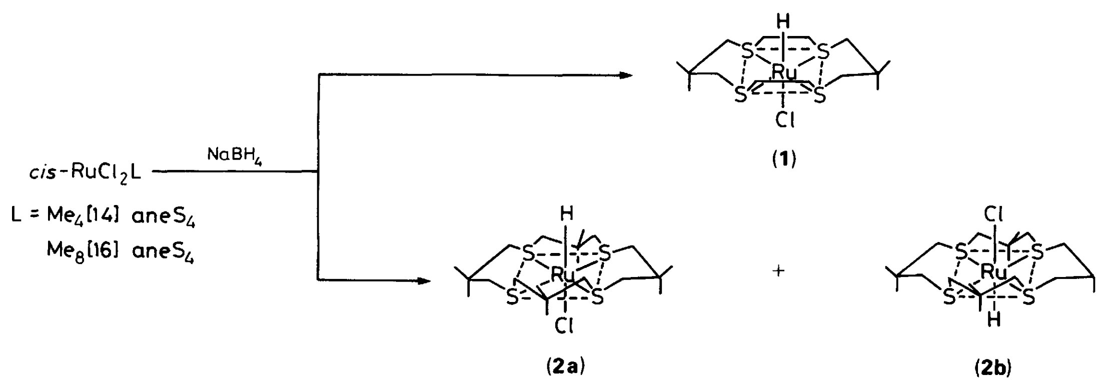
† Me_4[14]aneS_4 = 6,6,13,13-tetramethyl-1,4,8,11-tetrathiacyclotetradecane, Me_8[16]aneS_4 = 3,3,7,7,11,11,15,15-octamethyl-1,5,9,13-tetrathiacyclohexadecane.

‡ Satisfactory elemental analyses were obtained for (**1**) and (**2**). For (**1**) ^{1}H NMR (CD_2Cl_2) δ −23.1 (s, RuH), 1.12 and 1.24 (s, Me), 2.27 and 3.18 (d, *J* 10.5 Hz, S$CH_2$$Me_2$), 2.39 and 3.07 (m, S$CH_2$$CH_2$). For (**2**) ^{1}H NMR (CD_2Cl_2) δ −21.73 (s, RuH), 1.10 and 1.24 (s, Me), 2.27 and 3.18 (d, *J* 11.8 Hz, SCH_2), −21.64 (s, RuH), 1.08 and 1.24 (s, Me), 2.32 and 3.09 (d, *J* 11.0, SCH_2).



Scheme 1

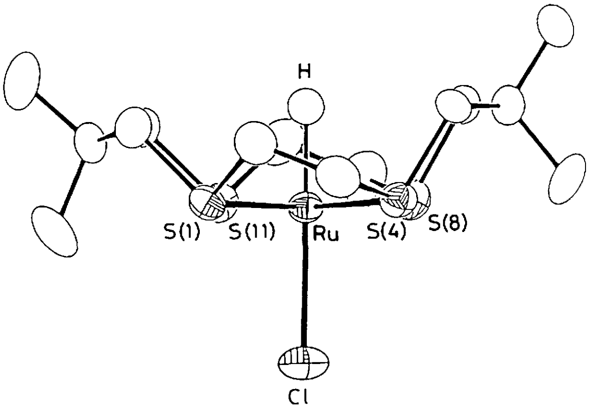


Figure 1. Molecular structure of (1) showing 50% thermal ellipsoids. Selected bond lengths (Å) and angles (°) are as follows: Ru–S(1) 2.280(2), Ru–S(4) 2.307(2), Ru–S(8) 2.308(2), Ru–S(11) 2.292(2); H–Ru–Cl 174.5(23), S(1)–Ru–S(4) 87.5(1), S(1)–Ru–S(11) 94.9(1), S(4)–Ru–S(8) 89.1(1), S(8)–Ru–S(11) 88.1(1), S(1)–Ru–S(8) 173.9(1), S(4)–Ru–S(11) 174.4(1).

(1958 cm^{-1}, Nujol mull) and a hydrido ^{1}H NMR signal [δ −23.1(s)], however, indicates the presence of only one isomer both in solution and in the solid state. The relative position of hydrido and chloro ligands at the axial sites with respect to the ring C atoms was determined unequivocally by a single crystal *X*-ray structural determination (Figure 1).§ The molecule of (**1**) is essentially octahedral with the mutually *trans* hydrido and chloro ligands. The hydrido ligand chooses the stereochemically congested axial site, while the chloro ligand co-ordinates on the uncongested site to prevent stereochemical repulsions with the ring CH$_2$ groups. The hydrido ligand is just in contact with the axial hydrogen atoms of ring C(5) and C(7) atoms, their respective non-bonded distances being 2.34(6) and 2.40(7) Å. The Ru–H [1.68(8) Å] and Ru–Cl distances [2.559(2) Å] are very similar to the corresponding values [1.65 and 2.549(1) Å] found for *trans*-RuH(Cl)(diop)$_2$, [diop = 2,2-dimethyl-4,5-bis(diphenylphosphinomethyl)-1,3-dioxolane].[4] The Ru–S distances [average 2.297(2) Å] are significantly shorter than the corresponding lengths *trans* to the S atoms [2.336(1) Å] in *cis*-RuCl$_2$[14]aneS$_4$,[5] suggesting a considerable compression of the Ru$^{\text{II}}$–S bonds by *syn*-Me$_4$[14]aneS$_4$ compared to the [14]aneS$_4$ in a folded form. This results in displacement of the Ru atom by 0.101(1) Å from the strict equatorial plane defined by the four S atoms (±0.001 Å) toward the Cl atom. Another structural feature may be the close contacts between the hydrido ligand and equatorial S atoms [2.72(7)—2.84(7) Å].

The spatial volume to accommodate a ligand at the congested axial site is expected to be dilated with increasing the ring size of crown thioether. Indeed, no site preference of the axial hydrido and chloro ligands was observed for the 16-membered crown thioether analogue (**2**). Complex (**2**) was prepared by treating *cis*-RuCl$_2$Me$_8$[16]aneS$_4$ with a stoicheiometric amount of NaBH$_4$ in EtOH at room temperature and was obtained as yellow crystals (51%).‡ The *syn* conformation of the co-ordinated Me$_8$[16]aneS$_4$ was confirmed by the ^{1}H NMR spectrum. Both IR [ν(Ru–H) 1860 and 1904 cm^{-1}, Nujol mull] and ^{1}H NMR data [δ_{RuH} −21.64(s) and −21.73(s)] show the presence of two geometrical isomers (**2a**) and (**2b**) (Scheme 1). The ratio of the two isomers is 2 : 3.

Finally, it is to be noted that the Mo(*syn*-Me$_8$[16]aneS$_4$) moiety in *trans*-Mo(N$_2$)$_2$(*syn*-Me$_8$[16]aneS$_4$)[6] also serves as a host in molecular recognition through co-ordination of π-acids possessing different steric demands at the axial sites. A novel example may be discrimination of the C=O and C=N bonds of PhNCO ligands in *trans*-Mo(η^2-O,C-PhNCO)(η^2-C,N-PhNCO)(*syn*-Me$_8$[16]aneS$_4$) where the ligand η^2-O,C-PhNCO, which is less bulky than η^2-C,N-PhNCO, co-ordinates specifically at the congested site, which will be published subsequently.

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§ *Crystal data* for (**1**): C$_{14}$H$_{29}$ClS$_4$Ru, orthorhombic, space group *Pna*2$_1$, a = 14.684(13), b = 12.605(2), c = 10.284(7) Å, U = 1904(2) Å^3, Z = 4, D_c = 1.61 g cm^{-3}, μ(Mo-K$_\alpha$) = 15.8 cm^{-1}. 3167 Unique reflections ($3 \leq 2\theta \leq 60°$) were collected on a Rigaku AFC-6 diffractometer using graphite monochromated Mo-K_α radiation; 2303 reflections with $|F_o| \geq 6\sigma(F_o)$ were used in the structure determination. The structure was solved by Patterson methods and refined by the block-diagonal least squares procedure. Refinement was carried out with anisotropic thermal parameters for all non-H atoms, with an isotropic thermal parameter for the hydrido H atom, and with fixed thermal and positional parameters for other H atoms to converge to $R(R_w)$ = 0.030(0.033), S = 1.29. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.