Crystal and Molecular Structure of *cis*-Dichloro(1,4,8,11-tetrathiacyclotetradecane)ruthenium(II) Dihydrate; A Correction to the Reported Stereochemistry based on Infrared Spectroscopy

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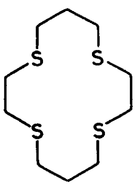
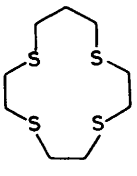
The crystal and molecular structure of *cis*-[RuL^{1}Cl$_2$]·2H$_2$O (L^1 = 1,4,8,11-tetrathiacyclotetradecane) has been solved by Patterson and Fourier methods. The crystals are monoclinic, space group $C2/c$, with a = 10.795(2), b = 17.541(3), c = 9.452(1) Å, β = 100.70(1)°, and Z = 4. Refinement by full-matrix least squares gave R = 0.038 for 2 094 diffractometer observations. This crystallographic determination disproves the previous assignment, based on i.r. spectroscopy, of a *trans*-configuration to this title complex. The importance of Ru $\longrightarrow$ S π back-bonding in this ruthenium(II) complex is manifested by the much shorter Ru–S bond distances when the sulphur atoms are *trans* to a chloride than when they are *trans* to each other. The i.r. spectra of this and some related complexes of L^1 and ruthenium(II) and ruthenium(III) are discussed.

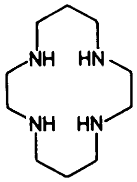
As part of the programme to investigate the chemistry of octahedral amine and thioether complexes of ruthenium(II) and ruthenium(III), Poon and Che [1] have recently reported the synthesis and characterization of some complexes with the macrocyclic thioether ligands L^1 (1,4,8,11-tetrathiacyclotetradecane) and L^2 (1,4,7,10-tetrathiacyclotridecane). The geometrical configuration of these complexes was assigned on the basis of far-i.r. spectroscopy. For [RuL^{1}Cl$_2$][ClO$_4$], a *trans* configuration was assigned,[1] based on the observation that the far-i.r. spectra of this and the corresponding complex [RuL^{1}Br$_2$][ClO$_4$] are nearly identical except that the band near 305 cm^{-1} is much more intense for the dichloro-complex while the band near 230 cm^{-1} is more intense for the dibromo-analogue. Accordingly, the band at 305 cm^{-1} was assigned as a ν(Ru–Cl) stretch and hence a *trans* configuration was assigned to the dichloro-complex. It was also suggested that the band at 230 cm^{-1} be assigned as a ν(Ru–Br) stretch although it was not clear if that was the only vibration since a second ν(Ru–Br) stretch might occur close to or below 200 cm^{-1} and this would fall outside our instrumental limit for detection.



L^1



L^2



L^3

Furthermore, a comparison of the corresponding far-i.r. spectra of [RuL^{1}Cl$_2$][ClO$_4$] and [RuL^{1}Cl$_2$]·2H$_2$O revealed the presence of only one ν(Ru–Cl) stretch at 250 cm^{-1} in the latter ruthenium(II) complex which was also assigned a *trans* configuration.[1] For the L^2 complexes, a *cis* configuration was assigned.[1]

However, these assignments of geometrical configuration are somewhat surprising. They would imply that the ruthenium(II) ion is even smaller than rhodium(III) and cobalt(III) ions, since the last two ions formed *cis*-L^1 complexes,[2] but is of about the same size as nickel(II) which gave *cis*-L^2 and *trans*-L^1 complexes.[3]

In order to confirm or to disprove the assignment of a *trans* configuration to these RuL^1 complexes, we have grown suitable crystals of [RuL^{1}Cl$_2$]·2H$_2$O and report here its crystal and molecular structure. The study is also very significant in its own right since very little is known about thioether complexes of ruthenium.[1,4,5] To our knowledge, this report represents the first paper on the crystal and molecular structure of a saturated thioether complex of ruthenium.

EXPERIMENTAL

Crystal Data.—[Ru(C$_{10}$H$_{20}$S$_4$)Cl$_2$]·2H$_2$O, M = 476.52, Monoclinic, space group $C2/c$, a = 10.795(2), b = 17.541(3), c = 9.452(1) Å, β = 100.70(1)°, U = 1 758.7 Å^3, D_m = 1.80$_6$ g cm^{-3}, Z = 4, D_c = 1.800 g cm^{-3}, $F(000)$ = 968, Mo-K_α radiation, λ = 0.710 69 Å, μ(Mo-K_α) = 16.11 cm^{-1}.

Bright orange prisms were obtained by slow evaporation of a solution of *cis*-[RuL^{1}Cl$_2$] in dilute aqueous HCl. Intensity data were collected from a crystal of approximately 0.2 × 0.15 × 0.3 mm on a Nicolet R3 diffractometer using the θ—2θ scanning technique with variable scan rate. All reflections within the $hk \pm l$ quadrants extending to 2θ = 55° were measured. Three check reflections were monitored continually and gave no indication of intensity loss during the 53 h of *X*-ray exposure. A total of 2 134 independent reflections were obtained of which 2 094 had net intensity (I) greater than zero. No correction was made for absorption.

Structure Determination and Refinement.—The positions of the ruthenium, chlorine, and two sulphur atoms were determined from a three-dimensional Patterson synthesis while the five carbon atoms and the oxygen atom of the water molecule were recovered from a subsequent Fourier map. The R index ($= \Sigma|\Delta F|/\Sigma|F_o|$) was 0.30.

Refinement was carried out mainly by full-matrix least-squares methods. The quantity minimized was $\Sigma w(F_o^2 - F_c^2)^2$, with weight, $w = 1/\sigma^2(F_o)^2$. Atomic scattering factors with the real part of anomalous dispersion applied to those for ruthenium, sulphur, and chlorine were obtained from International Tables.[6] Calculations were carried out on an IBM 3031 computer using the CRYM system.[7]

After several cycles of least-squares adjustment of the co-ordinates and anisotropic thermal parameters of the non-hydrogen atoms the R index was reduced to 0.056. At this stage positions of the hydrogen atoms were recovered from a difference-Fourier map. There were indications that the water molecule was disordered, hence two sets of hydrogen positions were chosen, each with an occupancy factor of 0.5. These hydrogen parameters were not adjusted in subsequent refinement.

TABLE 1

Fractional atomic co-ordinates ($\times 10^3$ for H, $\times 10^5$ for other atoms) with standard deviations in parentheses

Atom	x	y	z
Ru	0	18 815	25 000
S(1)	1 503(8)	9 408(5)	9 035(9)
S(2)	21 376(8)	19 412(5)	35 244(10)
Cl	4 263(9)	28 670(5)	7 847(11)
C(1)	11 463(38)	11 714(23)	55 663(41)
C(2)	23 221(36)	12 030(22)	49 174(42)
C(3)	31 340(37)	15 919(26)	23 151(47)
C(4)	26 956(39)	9 180(26)	13 600(49)
C(5)	15 610(38)	10 612(24)	1 495(42)
O	44 093(38)	3 316(19)	87 006(37)
H(1)	123(4)	77(3)	620(5)
H(2)	92(4)	166(2)	591(5)
H(3)	250(4)	70(2)	454(4)
H(4)	284(4)	127(3)	538(5)
H(5)	391(5)	154(3)	284(5)
H(6)	333(5)	197(2)	191(5)
H(7)	247(4)	51(2)	192(4)
H(8)	340(5)	71(3)	97(5)
H(9)	155(5)	67(3)	−63(5)
H(10)	155(4)	152(3)	−13(5)
H(11) *	370	30	800
H(12) *	450	85	885
H(13) *	490	30	800
H(14) *	480	10	960

* Assumed half populated site.

In the last least-squares cycle a list of 128 parameters was adjusted: atomic co-ordinates, anisotropic thermal parameters of the non-hydrogen atoms, isotropic thermal parameters of the hydrogen atoms, a scale factor, and a secondary extinction factor. The parameters of the hydrogen atoms were kept in one matrix and the rest of the parameters in another.

The final R index for 2 094 reflections was 0.038, ' the goodness of fit ', $[w(F_o^2 - F_c^2)^2/(m - s)]^{\frac{1}{2}}$, where m = 2 094 measurements and s = 128 parameters, was 2.46, and the final value of the secondary extinction parameter was $(0.28 \pm 0.03) \times 10^{-7}$. Atomic parameters are listed in Table 1. Observed and calculated structure factors and thermal parameters are in Supplementary Publication No. SUP 23301 (9 pp.).†

RESULTS AND DISCUSSION

An ORTEP drawing of the molecule is shown in Figure 1. Hydrogen bonds are formed by three of the four partial hydrogen atoms of the water molecule, as detailed in Table 2 and shown in Figure 2. The bond distances and angles are given in Table 3 (not included in the Table are the 10 C–H distances, average 0.90 ± 0.03 Å, and the 25 H–C–H angles, average 109 ± 1°).

The macrocyclic ligand L^1 has been known to give rise to two different modes of co-ordination. It behaves as a quadridentate ligand forming *endo*-complexes with either a planar disposition of the macrocycle, such as $[NiL^1][BF_4]_2$,[8] $[CuL^1][ClO_4]_2$,[9] and $[HgL^1(OH_2)][ClO_4]_2$,[10] or a folded configuration, such as *cis*-$[ML^1X_2]Y$ [2] (M = Co^{III} or Rh^{III}, X = halide ion, and Y = univalent counter ion). Conversely, though much less common, it can function as a bridging ligand, adopting an *exo*-configuration. It has been shown to act either as an unidentate bridging ligand, such as that occurring in $[(NbCl_5)_2L^1]$,[11] or as a bidentate bridging ligand in $[(HgCl_2)_2L^1]$,[10] see below. All these different types of co-ordination, with the exception of *endo-cis*, have been demonstrated crystallographically.[8-11] The present paper represents the first crystallographic evidence for an *endo-cis* mode of co-ordination of L^1 about a transition-metal ion.

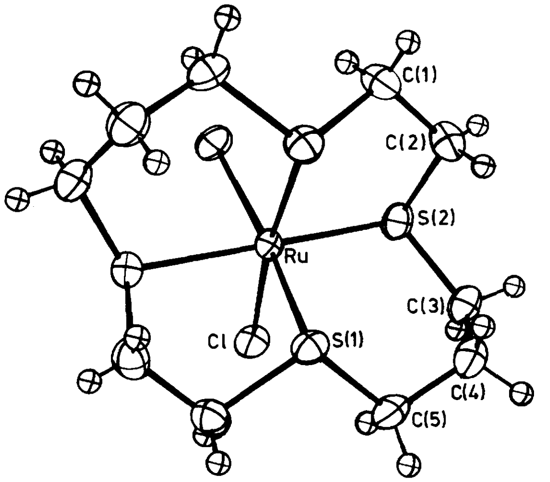
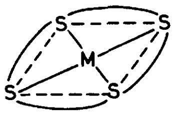
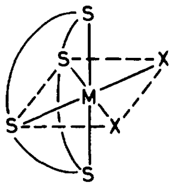


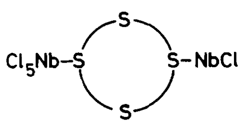
FIGURE 1 ORTEP drawing of *cis*-$[RuL^1Cl_2]\cdot 2H_2O$; thermal ellipsoids are drawn at 50% probability level



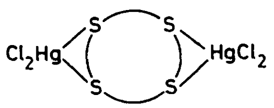
endo-planar



endo-cis



exo-unidentate bridge



exo-bidentate bridge

The configuration of the folded macrocycle L^1 is very similar to that of the nitrogen analogue L^3 (1,4,8,11-tetra-azacyclotetradecane) in *cis*-$[CoL^3(en)]Cl_3\cdot 3H_2O$ [12] (en = 1,2-diaminoethane) with the six-membered chelated rings adopting a chair conformation. However, the five-membered rings adopt a very distorted *gauche* con-

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† For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

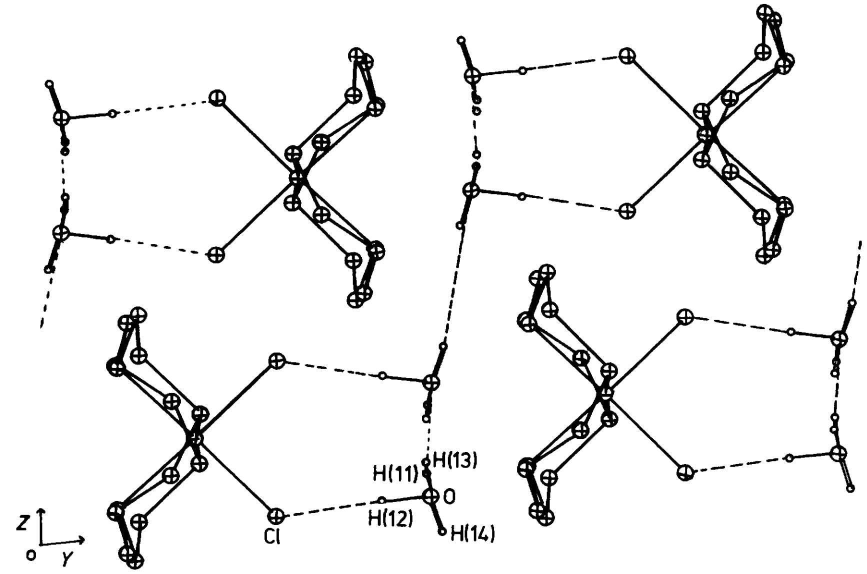

FIGURE 2 A drawing of the structure viewed approximately down the *a* axis

formation (Table 4). The lone pairs of electrons on the two *trans* sulphur atoms are pointing towards the two unidentate chloride ligands.

The most outstanding feature of the structure is a shorter Ru–S bond distance by *ca.* 0.071 Å when the sulphur atom [S(1) or S(1′)] is *trans* to a chlorine atom (Cl′ or Cl respectively) than when it is *trans* to another sulphur atom [S(2) and S(2′)]. This observation is a clear manifestation of the importance of Ru $\longrightarrow$ S π back-bonding in the stabilization of ruthenium(II) complexes.[1] When a sulphur atom is *trans* to a chlorine atom, it has full access to a filled *d* orbital; whereas when it is *trans* to another sulphur atom, it has to compete for the same filled *d* orbital with this other sulphur atom. Accordingly, it is to be expected that S(1) and S(1′) would form stronger Ru–S bonds than S(2) and S(2′). It thus appears that the folding of the macrocycle L^1 in metal complexes does not necessarily arise from the size effect of the central metal ions. The folding of L^1 will enhance the π back-bonding capability than will the planar disposition of the macrocycle where all four sulphur atoms are always *trans* to another sulphur atom, and this will result in a better stabilization of ruthenium(II) complexes.

TABLE 2

Hydrogen-bond distances and angles in the following general system O–H · · · A

H	A	O · · · A/Å	H · · · A/Å	O–H · · · A/°
H(12)	Cl [a]	3.197	2.28	176
H(13)	O [b]	2.802	1.89	167
H(14)	O [c]	2.802	1.84	178

[a] $\frac{1}{2} - x$, $\frac{1}{2} - y$, $1 - z$. [b] $1 - x$, y, $\frac{3}{2} - z$. [c] $1 - x$, $-y$, $2 - z$.

The present finding of a folded structure clearly disproves the previous assignment [1] of a *trans* configuration to this title complex. In fact, a closer look at the i.r. spectra of this and other complexes of L^1 ruthenium(II) and ruthenium(III) reported previously [1] in the region 800—950 cm^{-1}, which is most diagnostic for the assignment of geometrical configuration to L^3 complexes,[13,14] reveals a close resemblance to each other and to those of all known *cis*-L^3 complexes (Table 5). It is well known

TABLE 3

Bond distances and angles with standard deviations in parentheses *

(*a*) Distances (Å)

Ru–S(1)	2.262(1)
Ru–S(2)	2.333(1)
Ru–Cl	2.471(1)
S(1′)–C(1)	1.825(4)
C(1)–C(2)	1.510(6)
C(2)–S(2)	1.831(4)
S(2)–C(3)	1.815(4)
C(3)–C(4)	1.509(6)
C(4)–C(5)	1.534(6)
C(5)–S(1)	1.810(4)

(*b*) Angles (°)

S(1′)–Ru–S(1)	86.3(1)
S(1)–Ru–Cl	91.6(1)
Cl–Ru–Cl′	91.2(1)
S(2)–Ru–S(1′)	86.8(1)
S(2)–Ru–S(1)	97.0(1)
S(2)–Ru–Cl	87.2(1)
S(2)–Ru–Cl′	89.2(1)
Ru–S(1′)–C(1)	101.9(2)
S(1′)–C(1)–C(2)	106.4(3)
C(1)–C(2)–S(2)	109.3(3)
C(2)–S(2)–Ru	103.5(2)
C(2)–S(2)–C(3)	102.5(3)
Ru–S(2)–C(3)	112.3(2)
S(2)–C(3)–C(4)	119.0(3)
C(3)–C(4)–C(5)	115.9(4)
C(4)–C(5)–S(1)	107.5(3)
C(5)–S(1)–Ru	110.3(2)

* Primed atoms are atoms related by symmetry translation of $-x$, y, $\frac{1}{2} - z$.

TABLE 4

Deviations of the atoms from the least-squares planes (Å)

Plane 1: Ru, S(1′),* S(2)

$$-0.3275A + 0.6786B + 0.7069C + 3.910 = 0$$

[Ru 0.000, S(1′) * 0.000, S(2) 0.000, C(1) 0.799, C(2) −0.012]

Plane 2: S(1), S(2), C(3), C(5)

$$-0.1556A + 0.8825B - 0.4072C + 1.186 = 0$$

[S(1) −0.103, S(2) 0.103, C(3) −0.138, C(5) 0.138, Ru 0.764, C(4) −0.741]

* Symmetry transformations with respect to S(1) are $-x$, y, $\frac{1}{2} - z$.

TABLE 5

Infrared spectra in the region 800—950 cm^{-1} of some *trans* and *cis* complexes of L^1 and L^3

Complex	Absorption bands (cm^{-1})											
trans-[CoL^3Cl_2]Cl [a]	938w	918w		906s	888s						818s	
trans-[CrL^3Cl_2]Cl [b]	930vw		898vw	890s	882s						804s	
trans-[FeL^3Cl_2][ClO_4] [c]	932w	920w	905w	890s	888s (sh)						810m	
trans-[RuL^3Cl_2][ClO_4] [d]	938w	925w (sh)	902w	888s	878s						800s	
trans-[$RuL^3(NCS)_2$][ClO_4]·H_2O [d]	930w	920w	900w	888m	880m				824m [e]		810m (sh)	
cis-[CoL^3Cl_2]Cl [a]	930w			890w		872s	859s	841w		824w	808s	
cis-[CrL^3Cl_2]Cl [b]	930w			900vw		872m	862m (sh)	854m		815w	805m	
cis-[FeL^3Cl_2]Cl [c]	925m			892vw		866s	858m	850s		808m	794s	
cis-[RuL^3Cl_2]Cl [f]	930w			895w		868s	850s	840m (sh)		810m	800s	
cis-[$RuL^3(NCS)_2$][ClO_4]	932m			898w		864m	850m	845w (sh)	832w [e]	810m (sh)	802m	
cis-[$RuL^3(NCS)_2$]·H_2O [f]	930w			900w		862m	850m			810m (sh)	800s (sh)	780s [e]
cis-[RuL^1Cl_2][ClO_4] [g]		925m	905m			860s	842m			818m		
cis-[RuL^1Br_2][ClO_4] [g]		928m	907m			860s	840m			817m		
cis-[RuL^1Cl_2] [g]	930m	925m	910m			860s	850m			820m	815w	
cis-[RuL^1Br_2] [g]		925m	915m			865s	850m			820m	808w	
cis-[RuL^1I_2] [g]		928m	912m			865s	850m			820m	810w	
cis-[$RuL^1(NCS)_2$] [g]		922m	912m			870s	850m			820m (sh)	810s [e]	
cis-[$RuL^1(NO_2)_2$] [g]		930m	915m			870s	850m		825s [h]	820m (sh)	810w	
cis-[$RuL^1(N_3)_2$] [g]		930m	912m			870s	848m			828m	815w	
cis-[$RuL^1Cl(OH_2)$][ClO_4] [g]	930w (sh)	920m	905m			862s	845m			818m	810w	
cis-[$RuL^1Br(OH_2)$][ClO_4] [g]		925m	910m			867s	852m			820m		

[a] Ref. 13. [b] C. K. Poon and K. C. Pun, *Inorg. Chem.*, 1980, **19**, 568. [c] P. K. Chan and C. K. Poon, *J. Chem. Soc., Dalton Trans.*, 1976, 858. [d] C. K. Poon and C. M. Che, *Inorg. Chem.*, 1981, **20**, 1640. [e] ν(C–S) stretch of *N*-bonded thiocyanate ligand. [f] Ref. 14. [g] Ref. 1. [h] δ(NO_2) of *N*-bonded nitro-ligand.

that *trans*-L^3 complexes show two groups of bands separated by $\geqslant 70$ cm^{-1} whereas *cis*-L^3 complexes have at least five bands separated fairly evenly in the region 800—900 cm^{-1}.[13,14] Since the ligand conformation of L^1 is very similar to that of the known complex *cis*-[CoL^3(en)]$Cl_3 \cdot 3H_2O$,[12] it is not surprising to expect that the CH_2 skeletal vibrations are also rather similar. Since all $Ru^{II}L^1$ and $Ru^{III}L^1$ complexes reported[1] are prepared from this key title complex, *cis*-[RuL^1Cl_2]$\cdot 2H_2O$, under mild conditions, and as mentioned above they have very similar CH_2 skeletal vibrations, it seems, therefore, most likely that the previous assignment[1] of a *trans*-configuration to all these L^1 complexes was in error. They should all be reassigned as having a *cis* configuration.

Based on a *cis* configuration, a second ν(Ru–Cl) stretch for *cis*-[RuL^1Cl_2][ClO_4] and *cis*-[RuL^1Cl_2]$\cdot 2H_2O$ should be present. However, the weakness of all the far-i.r. bands, except that at 305 cm^{-1} for the former and that at 250 cm^{-1} for the latter, makes the identification of this second ν(Ru–Cl) stretch very difficult. It was essentially due to this apparent non-existence of this second ν(Ru–Cl) stretch that led us to predict wrongly the geometrical configuration of all the ruthenium–L^1 complexes.[1]

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