Structural and Mechanistic Studies of Co-ordination Compounds. Part 26.[1] Synthesis and Characterization of Some Octahedral Complexes of Ruthenium-(II) and -(III) with Macrocyclic Quadridentate Thioethers

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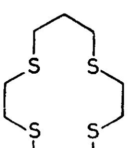
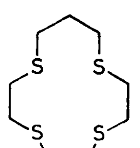
A series of ruthenium-(II) and -(III) complexes of the macrocyclic quadridentate thioethers 1,4,8,11-tetrathiacyclotetradecane (L^1) and 1,4,7,10-tetrathiacyclotridecane (L^2) has been prepared and characterized. Complexes containing the 14-membered ring, L^1, *viz. trans*-$[RuL^1X_2]^+$ (X = Cl or Br), *trans*-$[RuL^1X_2]$ (X = Cl, Br, I, NCS, N_3, or NO_2), and *trans*-$[RuL^1X(OH_2)]^+$ (X = Cl or Br), have the two remaining unidentate ligands *trans* to each other. However, the 13-membered ring, L^2, co-ordinates to the central metal ion in a folded manner to give *cis*-$[RuL^2Cl_2]^+$, *cis*-$[RuL^2X_2]$ (X = Cl, Br, I, NCS, NO_2, or N_3), and *cis*-$[RuL^2Cl(OH_2)]^+$. All the ruthenium(III) complexes are low spin and the ruthenium(II) complexes diamagnetic. They are all monomeric species. The electronic and i.r. absorption spectra of these complexes are discussed.

ALTHOUGH the chemistry of octahedral amine complexes of ruthenium-(II) and -(III) has been an area of active research,[1-3] relatively little work has been done on analogous thioether complexes. To our knowledge, only one thorough study on the synthesis of ruthenium complexes of saturated thioethers has been published,[4] but even this is limited to chloro- and bromo-complexes with uni- or bi-dentate thioethers. We have recently synthesized and studied the properties of a series of ruthenium complexes of macrocyclic quadridentate amines.[1,2,5-8] It is our intent to extend these studies to analogous complexes with the macrocyclic quadridentate thioethers 1,4,8,11-tetrathiacyclotetradecane (L^1) and 1,4,7,10-tetrathiacyclotridecane (L^2). This paper describes the preparation and characterization of the following complexes: *trans*-$[RuL^1Br_2]^+$, *trans*-$[RuL^1X_2]$ (X = Br, I, NCS, NO_2, or N_3), *trans*-$[RuL^1X(OH_2)]^+$ (X = Cl or Br), *cis*-$[RuL^2Cl_2]^+$, *cis*-$[RuL^2X_2]$ (X = Cl, Br, I, NCS, NO_2, or N_3), and *cis*-$[RuL^2Cl(OH_2)]^+$. The preparation of *trans*-$[RuL^1Cl_2]^{n+}$ (n = 0 or 1) has been reported previously.[1]



L^1



L^2

EXPERIMENTAL

1,4,8,11-Tetrathiacyclotetradecane [9] (L^1) and 1,4,7,10-tetrathiacyclotridecane [10] (L^2) were prepared by the literature methods. They were twice recrystallized before use. The salt $K_2[RuCl_5(OH_2)]$ was purchased from Johnson Matthey and Co. *trans*-Dichloro(1,4,8,11-tetrathiacyclotetradecane)-ruthenium(II) dihydrate and -ruthenium(III) perchlorate monohydrate were prepared by the published methods.[1]

trans-*Dibromo*(1,4,8,11-*tetrathiacyclotetradecane*)*ruthenium*(II).—An aqueous suspension (50 cm^3) of *trans*-$[RuL^1Cl_2]\cdot 2H_2O$ (1 g) and excess of NaBr (3 g) was refluxed for 3 h. The solution was filtered whilst hot and concentrated bromine-free HBr (10 cm^3) was added. The final solution was refluxed for another hour and was then concentrated to *ca*. 25 cm^3 using a rotary evaporator. On cooling, yellowish orange crystals slowly deposited. The product was recrystallized by the addition of excess of NaBr to a hot filtered solution of the complex (yield 70%).

trans-*Di-iodo*(1,4,8,11-*tetrathiacyclotetradecane*)*ruthenium*(II).—An aqueous solution (100 cm^3) of *trans*-$[RuL^1Cl_2][ClO_4]$ (0.5 g) and NaI (2 g) was refluxed for 1 h. Deep yellowish orange crystals slowly deposited as the reaction proceeded. The solution was cooled to increase the yield (70%). The corresponding trans-*di-isothiocyanate* was prepared by the same method with similar yield, except that Na[NCS] was used instead of NaI.

trans-*Dinitro*(1,4,8,11-*tetrathiacyclotetradecane*)*ruthenium*(II) *Monohydrate*.—An aqueous suspension (100 cm^3) of *trans*-$[RuL^1Cl_2]\cdot 2H_2O$ (0.5 g) and $Na[NO_2]$ (3 g) was heated at *ca*. 80 °C for 3 h with stirring. The solution was filtered whilst hot and then concentrated to *ca*. 25 cm^3. A pale yellow solid slowly crystallized out from the cooled solution (yield 55%).

trans-*Diazido*(1,4,8,11-*tetrathiacyclotetradecane*)*ruthenium*(II).—An aqueous suspension (100 cm^3) of *trans*-$[RuL^1Cl_2]\cdot 2H_2O$ (1 g) and $Na[N_3]$ (3 g) was refluxed for 2 h during which the solution turned yellow. It was filtered whilst hot and then concentrated to *ca*. 25 cm^3. On cooling, bright yellow crystals were obtained. The product was recrystallized by the addition of excess of $Na[N_3]$ to a hot filtered solution of the complex. On cooling, the desired product slowly crystallized (yield 75%).

trans-*Aquachloro*(1,4,8,11-*tetrathiacyclotetradecane*)*ruthenium*(II) *Perchlorate*.—This salt was prepared by dissolving *trans*-$[RuL^1Cl_2]\cdot 2H_2O$ in boiling dilute HCl (0.1 mol dm^{-3}). The solution was filtered and excess of $Na[ClO_4]$ was added. A light yellow solid was slowly deposited on cooling (yield 65%). The corresponding trans-*bromide* was prepared by the same method with similar yield by dissolving *trans*-$[RuL^1Br_2]$ in boiling bromine-free HBr (0.1 mol dm^{-3}).

trans-*Dibromo*(1,4,8,11-*tetrathiacyclotetradecane*)*ruthenium*(III) *Perchlorate*.—Concentrated $HClO_4$ (10 cm^3) was added to a hot solution (50 cm^3) of *trans*-$[RuL^1Br_2]$ (0.5 g) in HBr (0.1 mol dm^{-3}). The solution was heated on a steam-bath for *ca*. 2.5 h during which violet needle-shaped crystals deposited. The solution was cooled to increase the yield (60%).

Alternatively, a solution (40 cm^3) of *trans*-$[RuL^1Cl_2][ClO_4]$ (0.5 g) in dilute HBr (0.1 mol dm^{-3}) was heated on a steam-bath for *ca*. 2 h. The solution turned from deep red to violet-green. Concentrated $HClO_4$ (10 cm^3) was added and the solution was heated for another hour. Needle-shaped deep violet crystals slowly deposited, were filtered off (from the cooled solution), washed with a little cold water, acetone, and diethyl ether, and dried *in vacuo* at 78 °C (yield 50%).

cis-*Dichloro*(1,4,7,10-*tetrathiacyclotridecane*)*ruthenium*(II).—A suspension of $K_2[RuCl_5(OH_2)]$ (2 g) and L^2 (1.4 g) in 2-methoxyethanol (reagent grade, 25 cm^3) was refluxed for 30 h with stirring. A yellow solid gradually formed, which was filtered off, and washed with a small quantity of ice-cold water, acetone, and diethyl ether.

cis-*Dichloro*(1,4,7,10-*tetrathiacyclotridecane*)*ruthenium*(III) *Perchlorate*.—A hot solution (50 cm^3) of *cis*-$[RuL^2Cl_2]$ (1 g) in dilute HCl (2 mol dm^{-3}) was treated with concentrated $HClO_4$ (10 cm^3), then heated on a steam-bath for 2 h during which it turned deep red. The solution was filtered whilst hot and upon cooling, deep red needle-shaped crystals deposited (yield 70%).

cis-*Dibromo*(1,4,7,10-*tetrathiacyclotridecane*)*ruthenium*(II).—This was prepared as deep yellowish orange needle-shaped crystals by the same method as that for *trans*-$[RuL^1Br_2]$, except that crude *cis*-$[RuL^2Cl_2]$ was used as the starting material (yield 50%).

cis-*Aquachloro*(1,4,7,10-*tetrathiacyclotridecane*)*ruthenium*(II) *Perchlorate*.—This salt was prepared by dissolving *cis*-$[RuL^2Cl_2]$ in boiling dilute HCl (2 mol dm^{-3}, 25 cm^3). The solution was then filtered and addition of excess of $Na[ClO_4]$ precipitated out a yellow solid (yield 60%).

cis-*Di-isothiocyanato*(1,4,7,10-*tetrathiacyclotridecane*)-*ruthenium*(II).—An aqueous solution (50 cm^3) of *cis*-$[RuL^2Cl_2]$ (1 g) and Na[NCS] (1 g) was refluxed for 3 h. It was filtered whilst hot and excess of Na[NCS] added. On cooling a yellow solid appeared. This was recrystallized by dissolving in the minimum quantity of hot water, followed by addition of excess of Na[NCS] to the cooled solution (yield 70%). The corresponding cis-*di-iodide* was prepared by the same method with similar yield, except that NaI was used instead of Na[NCS].

The cis-*diazide* was also prepared using $Na[N_3]$ instead of Na[NCS]. This compound could be recrystallized by adding excess of $Na[N_3]$ to a filtered solution of the solid in the minimum amount of boiling water. On cooling deep orange crystals separated.

cis-*Dinitro*(1,4,7,10-*tetrathiacyclotridecane*)*ruthenium*(II).—An aqueous solution of $Na[NO_2]$ (6 g in 20 cm^3) was added to a hot filtered solution of *cis*-$[RuL^2Cl_2]$ (1 g in 25 cm^3), followed by heating on a steam-bath for 2 h. The solution was concentrated to *ca.* 25 cm^3 and then left at room temperature overnight. Yellow prismatic crystals appeared (yield 60%).

Elemental analytical data of all new complexes are collected in Table 1.

Physical Measurements.—Infrared spectra were recorded in Nujol mulls on a Perkin-Elmer 577 spectrophotometer (200—4 000 cm^{-1}). Electronic absorption spectra of freshly prepared solutions were obtained with a Beckman Acta CIII spectrophotometer. Magnetic susceptibilities of solid samples were measured by the Gouy method using mercury tetrathiocyanatocobaltate(II) as the calibrant.[11]

RESULTS AND DISCUSSION

The methods reported here for the synthesis of macrocyclic thioether complexes of ruthenium-(II) and -(III) are reproducible. In general, the parent dichlororuthenium(II) complexes are prepared by refluxing a stoicheiometric mixture of $K_2[RuCl_5(OH_2)]$ and the cyclic thioether (L^1 or L^2) in 2-methoxyethanol. The *cis*-$[RuL^2Cl_2]$ complex is very soluble in water and we have not been able to obtain an analytically pure sample. Analytical data showed that the complex was always contaminated with a small quantity of KCl which could not be removed after repeated recrystallization. Therefore, we have not included the analytical data of this complex in Table 1. However, this complex was pure enough to serve as the starting material for the synthesis of all other *cis*-$[RuL^2X_2]$ (X = Br, I, NCS, or N_3) and *cis*-$[RuL^2Cl(OH_2)]^+$ complexes by metathetical procedures. Furthermore, the i.r. data for *cis*-$[RuL^2Cl_2]$ are included in Tables 2 and 3 for comparison.

The dichlororuthenium(III) complexes were prepared by oxidizing the corresponding ruthenium(II) complexes with concentrated $HClO_4$ in the presence of excess of chloride. The dibromoruthenium(III) complexes could also be prepared by the same oxidation method or by displacing the co-ordinated chlorides from the corresponding dichlororuthenium(III) complexes by excess of bromide. However, *cis*-$[RuL^2Br_2]^+$ in solution is very unstable with respect to reduction to the corresponding ruthenium(II) complex. We have not been able to isolate an analytically pure sample of it and so we have not included the preparation in the Experimental section.

As for the preparation of other *trans*-dianionoruthenium(II) complexes of L^1, *trans*-$[RuL^1X_2]$, two general methods have been used. The first is a straightforward replacement of chlorides in *trans*-$[RuL^1Cl_2]\cdot 2H_2O$ by the appropriate anion. This method was applicable for the preparation of complexes with X = Br, NO_2, or N_3 and also for *trans*-$[RuL^1Cl(OH_2)]^+$. The starting material, *trans*-$[RuL^1Cl_2]\cdot 2H_2O$, is not very soluble in water and so efficient stirring was necessary in the course of refluxing the suspension of *trans*-$[RuL^1Cl_2]\cdot 2H_2O$ and excess of X^- in aqueous solution. This method was not suitable for the preparation of complexes with X = I or NCS since the products were usually contaminated with the relatively insoluble *trans*-$[RuL^1(Cl)X]$ which could not be easily removed. The second method employed *trans*-$[RuL^1Cl_2][ClO_4]\cdot H_2O$ as the starting material, which is soluble in water. The homogeneous reaction between this complex and an excess of X^- (X = I, NCS, NO_2, or N_3) led very efficiently to the formation of *trans*-$[RuL^1X_2]$. Reduction probably occurred during the second stage of the ligand-substitution reaction, *viz.* from *trans*-$[RuL^1(Cl)X]^+$ to *trans*-$[RuL^1X_2]$. This idea was supported by the observation that the preparation of *trans*-$[RuL^1X_2]$ (X = I or NCS) was not complicated by any insoluble intermediate, as described for the first method, which would have been the case if reduction had occurred in the first chloride-substitution step, giving the insoluble *trans*-$[RuL^1(Cl)X]$ as the intermediate.

The fact that the products are always in the ruthenium(II) oxidation state clearly indicated the importance of π back bonding in these macrocyclic thioether complexes. For corresponding complexes of saturated amines where such bonding is lacking, the reaction products are always in the III oxidation state.[1,5,8] Ruthenium(II) complexes of saturated amines are unstable with respect to their oxidation to ruthenium(III).[2]

TABLE 1

Analytical data (%) for some complexes of the type *cis*- or *trans*-[RuL(X)Y]Z

					Analysis [a]					
Configuration	L	X	Y	Z	C	H	S	Cl	Br	N
trans	L^1	Br	Br		22.6	4.05	23.9		30.1	
					(22.7)	(3.80)	(24.2)		(30.2)	
		Br	Br	ClO_4	18.8	3.35	20.4		25.3	
					(19.1)	(3.20)	(20.4)		(25.4)	
		I	I		19.5	3.25	20.7		*b*	
					(19.3)	(3.20)	(20.6)			
		Cl	OH_2	ClO_4	23.1	4.00	24.3	13.5		
					(23.0)	(4.20)	(24.5)	(13.6)		
		Br	OH_2	ClO_4	21.4	3.75	22.3	6.40	14.4	
					(21.2)	(3.90)	(22.6)	(6.25)	(14.1)	
		N_3	N_3		26.4	4.40	28.0			18.5
					(26.5)	(4.40)	(28.3)			(18.5)
		NCS	NCS		29.2	4.00	39.3			5.80
					(29.7)	(4.10)	(39.6)			(5.75)
		NO_2	NO_2	*c*	25.4	4.55	26.9			5.50
					(25.1)	(4.60)	(26.7)			(5.85)
cis	L^2	Cl	Cl	ClO_4	20.8	3.50	24.1	20.4		
					(20.6)	(3.40)	(24.4)	(20.3)		
		Cl	OH_2	ClO_4	21.3	3.80	24.7	14.4		
					(21.3)	(3.95)	(25.2)	(14.0)		
		Br	Br		21.4	3.70	24.5		31.0	
					(21.0)	(3.50)	(24.9)		(31.0)	
		I	I		17.9	3.15	20.7		*d*	
					(17.7)	(2.95)	(21.0)			
		N_3	N_3		24.5	4.25	29.0			18.9
					(24.6)	(4.10)	(29.2)			(19.1)
		NCS	NCS		27.9	4.00	40.6			6.05
					(28.0)	(3.80)	(40.8)			(5.95)
		NO_2	NO_2		24.5	4.05	28.6			6.25
					(24.2)	(4.05)	(28.6)			(6.25)

[a] Calculated values are given in parentheses. [b] I, 40.4 (40.8%). [c] Hydrate with one water molecule of crystallization. [d] I, 41.2 (41.7%).

TABLE 2

Far-i.r. spectra in the 200—360 cm^{-1} region of some *cis*- and *trans*-halogenoruthenium complexes of macrocyclic thioethers

Complex	Absorption bands (cm^{-1}) [a]					
trans-$[RuL^1Cl_2][ClO_4]$	355w	325w	*305s*		250w	230w
trans-$[RuL^1Br_2][ClO_4]$	350w	320w	300m		250w	*230m*
trans-$[RuL^1Cl_2]\cdot 2H_2O$	360w	325w	305w		*250s*	230m
trans-$[RuL^1Br_2]$	360w	325w	306w		250w	230w
trans-$[RuL^1I_2]$	355w	320w	305w		250w	225w
trans-$[RuL^1Cl(OH_2)][ClO_4]$	350w	330m	300m	*270m*	250w	230w
trans-$[RuL^1Br(OH_2)][ClO_4]$	360w	330w	300w		250w	230w
cis-$[RuL^2Cl_2][ClO_4]$		*330s*	*315s*	285m	250w	230w
cis-$[RuL^2Cl_2]$ [b]	360w	330w	307w	*270s*	*250s*	230w
cis-$[RuL^2Br_2]$	360w	335w	310w,	290w,br	250w	230w
cis-$[RuL^2I_2]$	360w	340w	310w	290w,br	250w	230w
cis-$[RuL^2Cl(OH_2)][ClO_4]$	360w	335w	310w	280w	*250s*	230w

[a] Bands assigned as ν(Ru–X) are italicized. Abbreviations: w = weak; m = medium; s = strong; br = broad; sh = shoulder. [b] Probably contaminated with KCl (see text).

All the new complexes are highly coloured and give well formed crystals which appear to be stable indefinitely in the solid state. In solution, the ruthenium(III) complexes are easily reduced to ruthenium(II). The magnetic moments and molar conductivities confirm that all the ruthenium(III) complexes are low-spin and that the ruthenium(II) complexes are diamagnetic monomeric species. [$\mu_{\text{eff.}}$ (23 °C) *ca.* 2.1 B.M.* for ruthenium(III) complexes and *ca.* 0 for ruthenium(II) complexes]. Λ in dimethyl sulphoxide–water (3 : 7 v/v) was *ca.* 100 Ω^{-1} cm^{2} mol^{-1} for all aquahalogenoruthenium(II) complexes; all other ruthenium(II) complexes were virtually non-electrolytes. [The experimental reading of Λ for all ruthenium(III) complexes gradually changed from the initial value of *ca.* 100 Ω^{-1} cm^{2} mol^{-1}, indicating that chemical reactions were taking place.]

The geometrical configuration of these complexes was assigned on the basis of i.r. spectroscopy. The far-i.r. spectra of the halogeno-complexes in the 200—360 cm^{-1} region of interest are collected in Table 2. A previous comparison of the corresponding far-i.r. spectra of $[RuL^1Cl_2][ClO_4]\cdot H_2O$ and $[RuL^1Cl_2]\cdot 2H_2O$ enabled the

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* Throughout this paper: 1 B.M. ≈ 9.27 × 10^{-24} A m^{2}.

assignment of the ν(Ru–Cl) stretch to be made.[1] In both cases, only one such stretch was observed (at 305 and 250 cm^{-1} respectively) and these complexes were thus assigned a *trans* configuration.[1] In fact, a shift of 55 cm^{-1} is about right for a change of one unit of formal positive charge from ruthenium(III) to ruthenium(II). The availability of the corresponding dibromo-complexes now unambiguously confirms the previous assignment [1] of ν(Ru–Cl) in the dichloro-complexes. A comparison of the corresponding spectra of $[RuL^1X(OH_2)][ClO_4]$ (X = Cl or Br) also showed that the ν(Ru–Cl) stretch occurs at 270 cm^{-1}. Unfortunately, our instrument did not allow us to measure far-i.r. spectra below 200 cm^{-1} and hence we could not determine ν(Ru–I) and ν(Ru^{II}–Br). Although we could assign with confidence the band at 230 cm^{-1} to ν(Ru–Br) for $[RuL^1Br_2][ClO_4]$, we could not say whether this is the only vibration since a second ν(Ru–Br) stretch may occur close to or below 200 cm^{-1}.

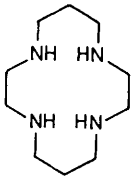
TABLE 3

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

Complex	Absorption bands (cm^{-1})									
trans-$[RuL^1Cl_2][ClO_4]$			925m	905m	860s	842m		818m		
trans-$[RuL^1Br_2][ClO_4]$			928m	907m	860s	840m		817m		
trans-$[RuL^1Cl_2]$		930m	925m	910m	860s	850m		820m		815w
trans-$[RuL^1Br_2]$			925m	915m	865s	850m		820m		808w
trans-$[RuL^1I_2]$			928m	912m	865s	850m		820m		810w
trans-$[RuL^1(NCS)_2]$			922m	912m	870s	850m		820m (sh)		*810s* [a]
trans-$[RuL^1(NO_2)_2]$			930m	915m	870s	850m	*825s* [b]	820m (sh)		810w
trans-$[RuL^1(N_3)_2]$			930m	912m	870s	848m		828m		815w
trans-$[RuL^1Cl(OH_2)][ClO_4]$		930w (sh)	920m	905m	862s	845m		818m		810w (sh)
trans-$[RuL^1Br(OH_2)][ClO_4]$			925m	910m	867s	852m		820m		
cis-$[RuL^2Cl_2][ClO_4]$	950m	935m		910s	862s	855s	842m	835m (sh)		812w
cis-$[RuL^2Cl_2]$ [c]	950m	940m		915m	860s		840m	835m		805m
cis-$[RuL^2Br_2]$	946w	932m		915m	870s	855s	840s			810w
cis-$[RuL^2I_2]$	940w	925m		910w (sh)	865s	860s	840s	820m		810w
cis-$[RuL^2(NCS)_2]$	945m	930m		915m	860s		838s			*807s* [a]
cis-$[RuL^2(NO_2)_2]$	945m	930w		915m	860s		842m	*820s* [b]	*815s* [b]	808w
cis-$[RuL^2(N_3)_2]$	945w	930w		915m	865s	857s	840s	835m (sh)		808w
cis-$[RuL^2Cl(OH_2)][ClO_4]$	945w	935s		915s	860s	852s		835m		800w

[a] Assigned as ν(C–S). [b] Arises from δ(NO_2). [c] Probably contaminated with KCl (see text).

However, a *trans* configuration could be assigned to all L^1 complexes by comparing their i.r. spectra in the 800—950 cm^{-1} region (Table 3). This region has been found particularly useful for the differentiation of *cis* and *trans* isomers of 1,4,8,11-tetra-azacyclotetradecane (L^3) complexes.[1,12] Clearly, the i.r. spectra in this region are virtually identical for all L^1 complexes reported here and hence all these complexes probably assume the same geometical configuration, *i.e.* *trans*, as the dichloro-complexes. This assignment was supported by the n.m.r. spectrum of $[RuL^1Br(OH_2)][ClO_4]$ in dimethyl sulphoxide. The CH_2 resonance was very similar to that of known *trans*-$[CoL^2X_2]^+$ complexes but was distinctly different from that of their *cis* isomer.[13]



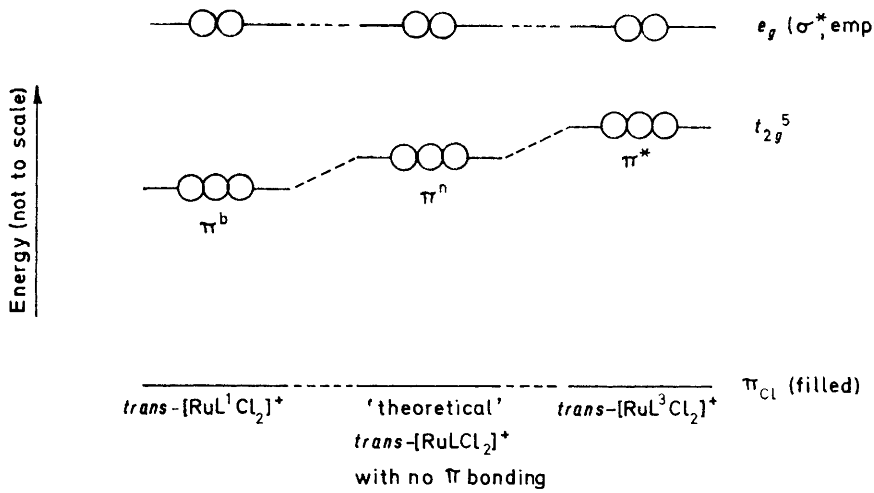
L^3

Using the same i.r. technique, a *cis* configuration could be assigned to all L^2 complexes prepared here. The far-i.r. spectra showed two ν(Ru–Cl) stretches for $[RuL^2Cl_2][ClO_4]$ (330 and 315 cm^{-1}) and $[RuL^2Cl_2]$ (270 and 250 cm^{-1}), and all these L^2 complexes had virtually identical i.r. spectra in the 800—950 cm^{-1} region. The ν(Ru–Cl) stretch for *cis*-$[RuL^2Cl(OH_2)][ClO_4]$ occurred at 250 cm^{-1}.

The results obtained indicate that the ring size of the 13-membered L^2 ligand is not large enough to hold the ruthenium(II) ion in a planar configuration, in contrast to that of the 14-membered L^1 ligand. This seems to imply that the ruthenium(II) is, surprisingly, even smaller than rhodium(III) and cobalt(III), since the last two ions formed *cis*-L^1 complexes,[14] but is of about the same size as nickel(II) which gave *cis*-L^2 and *trans*-L^1 complexes.[9]

An examination of the i.r. spectra showed that the ambidentate thiocyanate ligand is *N*-bonded in both L^1 and L^2 complexes. All these complexes, with the exception of the two isothiocyanates, have a weak absorption band near 810 cm^{-1}. The relatively strong absorption bands at 810 and 807 cm^{-1} for the L^1 and L^2 di-isothiocyanato-complexes respectively were taken to represent the *N*-bonded ν(C–S) stretch of the ligand.[15] The ν(C–N) stretching frequencies at 2 100 for the L^1 and at 2 100 and 2 060 cm^{-1} for the L^2 complexes were not sufficiently diagnostic for differentiation purposes. Unfortunately, we have not been able to assign any band to ν(Ru–NCS) in the far-i.r. spectra of these two isothiocyanato-complexes in order to substantiate the above assignment of the *N*-bonding mode. As for the two dinitro-complexes, they are clearly *N*-bonded, as shown by a multiplet in the 1 250—1 400 cm^{-1} region corresponding to $\nu_{asym}(NO_2)$ and $\nu_{sym}(NO_2)$, δ(NO_2) vibrations near 820 cm^{-1} (825 for the L^1 and 820 and 815 cm^{-1} for the L^2 complex), and a NO_2 rocking vibration near 600 cm^{-1}.

The electronic absorption spectra of these thioether complexes in dimethyl sulphoxide are collected in Table 4. It has been argued previously,[1] by comparing the spectra of *trans*-$[RuL^1Cl_2]^+$ and *trans*-$[RuL^1Cl_2]$ [*i.e.* ruthenium(III) against ruthenium(II)], that the band of the former at 560 nm must be a ligand-to-metal charge-transfer transition. This band was then assigned to a $\pi_S \rightarrow t_{2g}$ type transition by noting that most $\pi_{Cl} \rightarrow t_{2g}$ transitions of all known *trans*-dichlororuthenium complexes of saturated tetramines occurred near 350 nm.[1] Now, with the availability of *trans*-$[RuL^1Br_2][ClO_4]$, it seems that the previous assignment of the $\pi_S \rightarrow t_{2g}$ transition of *trans*-$[RuL^1Cl_2]^+$ to the lowest-energy band at 560 nm was in error. If the previous assignment had been correct there should not have been such a great 'red' shift of $\lambda_{max.}$ from *trans*-$[RuL^1Cl_2]^+$ to *trans*-$[RuL^1Br_2]^+$ (623 nm); indeed, $\lambda_{max.}$ should have been roughly independent of the nature of the halides. These lowest-energy bands should, therefore, be more correctly assigned as $\pi_X \rightarrow t_{2g}$ transitions (X = Cl or Br).



Effect of π bonding on the energy level of the t_{2g} orbitals (π^n level) of the central ruthenium(III) ion of *trans*-$[RuLCl_2]^+$ (L = L^1 or L^3)

TABLE 4

Visible and u.v. absorption spectra of some ruthenium complexes of macrocyclic tetrathioethers in dimethyl sulphoxide

Complex	$\lambda_{max.}$/nm [a]
trans-$[RuL^1Cl_2]\cdot 2\ H_2O$	*ca.* 430br(sh) (*ca.* 124), 363 (1 015), 304 (984)
trans-$[RuL^1Br_2]$	*ca.* 450br(sh) (*ca,* 130), 369 (992), 303 (943)
trans-$[RuL^1I_2]$	*ca.* 455br(sh) (*ca.* 180), 380 (896), 306 (2 130)
trans-$[RuL^1(N_3)_2]$	*ca.* 430(sh) (*ca.* 254), 363 (1 690), 310(sh) (1 360)
trans-$[RuL^1(NCS)_2]$	*ca.* 430(sh) (*ca.* 450), 345 (1 680)
trans-$[RuL^1(NO_2)_2]\cdot H_2O$	312 (2 800)
trans-$[RuL^1Cl(OH_2)][ClO_4]$	370 (890), *ca.* 340(sh) (700)
trans-$[RuL^1Br(OH_2)][ClO_4]$	376 (870), 340 (770)
trans-$[RuL^1Cl_2][ClO_4]\cdot H_2O$ [b]	560 (932), *ca.* 485br(sh) (740), 424 (1 350), *ca.* 350(sh) (1 620), 323 (2 050)
trans-$[RuL^1Br_2][ClO_4]$	623 (2 013), 472 (1 200), 380 (1 700), 335 (1 780)
cis-$[RuL^2Br_2]$	395 (780), 345(sh) (475)
cis-$[RuL^2I_2]$	405 (900), 320(sh) (1 040)
cis-$[RuL^2(N_3)_2]$	410 (1 640)
cis-$[RuL^2(NCS)_2]$	383 (1 600)
cis-$[RuL^2(NO_2)_2]$	308 (1 950)
cis-$[RuL^2Cl(OH_2)][ClO_4]$	387 (998), 350(sh) (630)
cis-$[RuL^2Cl_2][ClO_4]$	518 (2 120), 380 (2 620)

[a] Molar absorption coefficients (ϵ/dm^3 mol^{-1} cm^{-1}) are given in parentheses. [b] In dilute aqueous HCl; ref. 1.

It now remains to explain the red shift of this type of $\pi_{Cl} \rightarrow t_{2g}$ transition from tetramine complexes, such as *trans*-$[RuL^3Cl_2]^+$ (357 nm), to the corresponding tetrathioether complexes, such as *trans*-$[RuL^1Cl_2]^+$ (560 nm). Using a simple model of octahedral symmetry (neglecting axial-ligand distortion) and assuming that the level π_{Cl} is approximately the same in the two complexes, it is possible to explain the observed red shift in terms of π-bonding effects. As illustrated in the Figure, the t_{2g} level of the L^3 complex becomes antibonding (π^*) as a consequence of the ligand-to-metal π bonding and hence the energy of transition from π_{Cl} to t_{2g} (π^*) is increased relative to the 'theoretical' complex with no π bonding. On the other hand, since the t_{2g} level of the L^1 complex could become stabilized (π^b) if the metal-to-ligand (sulphur) π back bonding is more important than the ligand (chloride)-to-metal π bonding, a lower transition energy is expected. The combined effect is such that the $\pi_{Cl} \rightarrow t_{2g}$ transition energy is smaller and hence the $\lambda_{max.}$ larger for the L^1 than the L^3 complex.

As for the ruthenium(II) complexes, most of the *trans*-L^1 complexes show a broad shoulder in the visible region. Apparently, it seems reasonable to assume that these are ligand-field transitions, ${}^1A_{1g} \rightarrow {}^1T_{1g}$, of octahedral parentage. However, all the *cis*-L^2 complexes do not give such broad shoulders. With reference to the ligand-field bands of *cis*-$[RhL^1X_2]^+$ [X = Cl, λ 350 (ϵ 2 270); Br, 370 (2 180); and I, 405 nm (2 460 dm^3 mol^{-1} cm^{-1})],[14] it is possible that the lowest-energy bands reported (Table 4) for *cis*-L^2 complexes are ligand-field transitions. Accordingly, it is likely that the more intense bands near 350 and 305 nm are spin-allowed ligand-field transitions of the *trans*-L^1 complexes. In fact, the real intensities of the broad shoulders, after subtracting the contribution from the tailing of the more intense bands, should be rather small. It is thus more probable that these weak transitions correspond to spin-forbidden transitions.

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