Structural and Mechanistic Studies of Co-ordination Compounds. Part 25.[1] Synthesis and Characterization of Some Octahedral Halogeno-amine and -thioether Complexes of Ruthenium-(II) and -(III)

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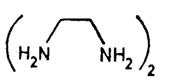
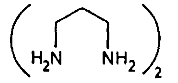
The published methods for the syntheses of *trans*-$[RuLCl_2]^+$ [L = L^1, bis(ethane-1,2-diamine); L^4, 3,7-diazanonane-1,9-diamine; or L^7, 1,4,8,11-tetra-azacyclotetradecane] have been modified. The modified method is highly efficient and reproducible and it has been employed to prepare other *trans*-$[RuLCl_2]^+$ complexes [L = L^2, bis(propane-1,3-diamine); L^3, bis(*NN'*-dimethylethane-1,2-diamine); L^5, 4,7-diazadecane-1,10-diamine; or L^6, 4,8-diazaundecane-1,11-diamine]. Other dihalogeno-complexes, *trans*-$[RuLBr_2]^+$ (L = L^1, L^2, L^4, or L^7) and *trans*-$[RuLI_2]^+$ (L = L^1 or L^4), have been prepared from their corresponding dichloro-complexes through the reactive ruthenium(II) intermediates. Mixed halogeno-complexes of the type *trans*-$[RuL^1(X)Y]^+$ [(X)Y = (Cl)Br, (Cl)I, or (I)Br] have been prepared by metathetical procedures. Meanwhile, some macrocyclic quadridentate thioether complexes *trans*-$[RuLCl_2]\cdot 2H_2O$ (L = L^8, 1,4,8,11-tetrathiacyclotetradecane; or L^9, 3,6,10,13-tetrathiabicyclo[13.4.0]nona-1,16,18-triene) and *trans*-$[RuL^8Cl_2][ClO_4]\cdot H_2O$ have also been synthesized. All these complexes are low-spin monomeric species. The electronic and i. absorption spectra of these complexes are discussed.

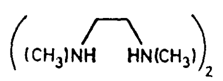
THE chemistry of ruthenium(III) amine complexes has been an area of active research.[2] However, relatively little work has been done on *trans*-$[RuL(X)Y]^{n+}$ type complexes, where L represents either two bidentate or one quadridentate amine ligand and X and Y are unidentate aniono-ligands, probably because a general and convenient synthetic route to these complexes has not yet been fully developed. We have recently reported [3,4] the syntheses of *trans*-$[RuLCl_2]^+$ [L = L^1, bis(ethane-1,2-diamine); L^4, 3,7-diazanonane-1,9-diamine; and L^7 = 1,4,8,11-tetra-azacyclotetradecane]. However, the method is time-consuming, and, occasionally, difficulties are encountered in isolating pure samples of the complexes in large enough quantities to be used as starting materials for the preparation of analogous aniono-amine complexes. Broomhead *et al.*[5] have also reported the syntheses of *trans*-$[RuL^1X_2]^+$ (X = Cl or Br) by the isomerization of the corresponding *cis* isomers. Again, the overall yield, taking into account the large number of steps involved in the synthetic processes starting from either $RuCl_3$ or $K_2[RuCl_5(OH_2)]$, is low and the method is not a general one for the direct syntheses of other *trans*-$[RuL(X)Y]^{n+}$ complexes.



L^1



L^2



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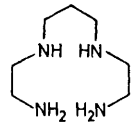

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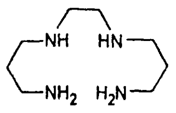
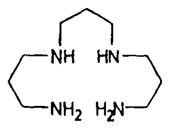
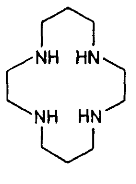


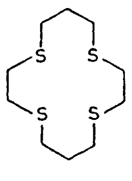
L^5



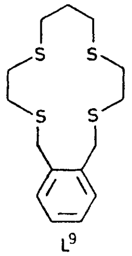
L^6



L^7



L^8



L^9

Our desire to study the photochemical, electrochemical, and thermal substitution reactions of these complexes over a wider range of L, X, and Y has prompted us to re-examine our synthetic method in greater detail. The modified method which we now report is reproducible and much more efficient. It is also a general method for the syntheses of other *trans*-$[RuLCl_2]^+$ complexes starting from $K_2[RuCl_5(OH_2)]$ [L = L^2, bis(propane-1,3-diamine); L^3, bis(*NN'*-dimethylethane-1,2-diamine); L^5, 4,7-diazadecane-1,10-diamine; and L^6, 4,8-diazaundecane-1,11-diamine]. Some other dihalogeno- and mixed halogeno-complexes are also prepared. At the same time, effort has also been devoted to the synthesis of some ruthenium complexes with macrocyclic quadridentate thioethers L^8 (1,4,8,11-tetrathiacyclotetradecane) and L^9 (3,6,10,13-tetrathiabicyclo[13.4.0]nona-1,16,18-triene), *viz. trans*-$[RuLCl_2]\cdot 2H_2O$ (L = L^8 or L^9) and *trans*-$[RuL^8Cl_2][ClO_4]\cdot H_2O$. Nickel(II),[6,7] cobalt(III),[8] and rhodium(III) [8] derivatives of L^8 and L^9 have been reported by Busch and co-workers.

EXPERIMENTAL

trans-*Dichlorotetraminеruthenium*(III) *Perchlorate*, *trans*-$[RuLCl_2][ClO_4]$ (L = L^{1-7}).—These complexes were prepared by essentially the same method, with similar yields. This method is described in detail below for L = L^1. A methanolic solution (250 cm^3) of L^1 (0.6 g, 0.01 mol) was added dropwise to a suspension of $K_2[RuCl_5(OH_2)]$ (2 g, 0.005 mol) in methanol (150 cm^3) (preferably absolute methanol) under reflux and with vigorous stirring. The addition process took *ca.* 6 h for completion. After further heating under reflux (1.5 h), the yellowish brown solution was filtered to remove the undissolved $K_2[RuCl_5(OH_2)]$ and the clear solution was evaporated to dryness. The brown solid was dissolved in a minimum quantity of dilute hydrochloric acid. Dropwise addition of a concentrated solution of $Na[ClO_4]$ precipitated out a yellowish orange solid which was filtered off and washed with a small volume of hot water to remove any $K[ClO_4]$ which had co-precipitated. The compound was finally recrystallized from dilute hydrochloric acid as bright orange crystals (yield 1.5 g, 70%). The purity of the complex, apparent from the size of the well shaped crystals, was confirmed by comparing its electronic absorption spectrum with that of an authentic sample. For the preparation of other *trans*-dichloro-complexes, doubly redistilled or recrystallized amines were used. In most cases, yellowish orange well shaped needles were obtained from dilute hydrochloric acid. Elemental analytical data of all new complexes are collected in Table 1.

TABLE 1

Analytical data for some complexes of the type *trans*-[RuL(X)Y]Z synthesized in this work

L	X	Y	Z	Analysis (%) [a] C	H	N	S	Cl	Br	I
L^1	Br	Br	ClO_4	10.0 (9.95)	3.35 (3.35)	11.7 (11.7)		7.4 (7.40)	33.3 (33.4)	
	I	I	I [b]	7.85 (7.55)	2.90 (3.15)	9.05 (8.85)				59.7 (59.7)
	Cl	Br	ClO_4	11.3 (11.0)	3.70 (3.70)	12.6 (12.8)		16.5 (16.3)	18.6 (18.3)	
	Cl	I	ClO_4	9.75 (9.95)	3.15 (3.30)	11.2 (11.6)		14.8 (14.7)		26.5 (26.3)
	Br	I	ClO_4	9.50 (9.10)	3.2 (3.05)	10.7 (10.6)			15.4 (15.2)	24.5 (24.1)
L^2	Cl	Cl	ClO_4	17.4 (17.2)	4.75 (4.75)	13.3 (13.4)		25.4 (25.4)		
	Br	Br	ClO_4	14.4 (14.2)	3.95 (3.95)	11.2 (11.0)		7.3 (7.0)		
L^3	Cl	Cl	ClO_4	21.5 (21.5)	5.25 (5.35)	12.5 (12.5)		23.9 (23.8)		
L^4	Br	Br	ClO_4	16.8 (16.2)	4.10 (3.85)	10.4 (10.8)			30.7 (30.7)	
	I	I	I	12.8 (13.1)	3.15 (3.10)	8.7 (8.75)				59.4 (59.4)
L^5	Cl	Cl	ClO_4	21.6 (21.6)	4.90 (4.95)	12.6 (12.6)		24.1 (23.9)		
L^6	Cl	Cl	ClO_4	23.7 (23.5)	5.20 (5.20)	12.3 (12.2)		23.3 (23.2)		
L^7	Cl	Cl	ClO_4	25.7 (25.5)	5.00 (5.15)	11.9 (11.9)		22.6 (22.6)		
	Br	Br	Br	22.6 (22.2)	4.35 (4.45)	10.3 (10.4)			44.2 (44.3)	
L^8	Cl	Cl	ClO_4 [c]	21.5 (21.5)	3.65 (3.95)		23.6 (23.7)	18.9 (19.1)		
	Cl	Cl	*b*	25.3 (25.2)	4.75 (5.05)		26.6 (26.9)	15.0 (14.9)		
L^9	Cl	Cl	*b*	33.8 (33.4)	4.40 (4.40)		23.8 (23.8)	13.4 (13.2)		

[a] Calculated values are given in parentheses. [b] Hydrate, with two H_2O of crystallization. [c] This complex is a hydrate with one H_2O of crystallization.

trans-*Dichloro*(1,4,8,11-*tetra-azacyclotetradecane*)-*ruthenium*(III) *Chloride*.—The perchlorate salt of this complex was very insoluble in water so the chloride was prepared instead, by essentially the same technique of dropwise addition of a methanolic solution of L^7 to a methanolic suspension of $K_2[RuCl_5(OH_2)]$, refluxing, filtering, and then evaporating the filtrate to a brown residue. The crude brown solid was dissolved in the minimum amount of boiling HCl (0.1 mol dm^{-3}). The hot solution was filtered, concentrated HCl (*ca.* 3 cm^3) was added to the filtrate, and the resulting solution was set aside to cool. Light brown leaflets which slowly formed were filtered off, washed with ethanol and diethyl ether, and dried *in vacuo* at 78 °C (yield 75%). The absorption spectrum of this complex was identical to that of an authentic sample.[3]

trans-*Dibromotetramineruthenium*(III) *Perchlorate*, *trans*-$[RuLBr_2][ClO_4]$ (L = L^1, L^2, *or* L^4).—These complexes were prepared by adding several pieces of zinc (1—2 g) to a hot solution of the corresponding *trans*-$[RuLCl_2][ClO_4]$ in bromine-free hydrobromic acid. The mixture was heated for *ca.* 1 h on a steam-bath and was then filtered while hot. To the filtrate was added a concentrated solution of $Na[ClO_4]$ (1—2 cm^3). Reddish brown needles slowly appeared on cooling, which were collected, washed with alcohol and diethyl ether, and dried *in vacuo* at 78 °C. The complex so obtained is in general pure enough, but it could be recrystallized, if desired, from dilute bromine-free hydrobromic acid (0.1 mol dm^{-3}) (yield 70%).

The salt *trans*-$[RuL^1Br_2][ClO_4]$, on the other hand, could be more conveniently prepared by treating a hot aqueous solution of *trans*-$[RuL^1Cl_2][ClO_4]$ directly with an excess of NaBr. The resulting solution was heated on a steam-bath for *ca.* 1 h. Concentrated bromine-free hydrobromic acid (4 cm^3) was added, followed by a few drops of a concentrated aqueous solution of $Na[ClO_4]$. Reddish brown *trans*-$[RuL^1Br_2][ClO_4]$ slowly crystallized out and could be recrystallized from dilute bromine-free hydrobromic acid (0.1 mol dm^{-3}) to give large prismatic red crystals (yield 75%).

trans-*Dibromo*(1,4,8,11-*tetra-azacyclotetradecane*)-*ruthenium*(III) *Bromide*.—This complex was prepared by the same zinc-reduction method as other dibromo-complexes described above except that here *trans*-$[RuL^7Cl_2]Cl$, instead of its perchlorate, was used as the starting material. After the reaction between the dichloro-complex and zinc in hydrobromic acid was complete, the hot filtrate was concentrated to *ca.* $\frac{2}{3}$ of its original volume and the solution was then set aside to cool. A bright orange microcrystalline solid slowly appeared which was recrystallized from dilute bromine-free hydrobromic acid (0.1 mol dm^{-3}) (yield 70%).

trans-*Di-iodotetramineruthenium*(III) *Iodide*, *trans*-$[RuL^1I_2]I\cdot2H_2O$ *and trans*-$[RuL^4I_2]I$.—These complexes were prepared by essentially the same zinc-reduction technique as their *trans*-$[RuLBr_2][ClO_4]$ analogues except that here NaI in toluene-*p*-sulphonic acid or iodine-free HI was used. After the reaction mixture was heated on a steam-bath for *ca.* 1 h, the hot filtrate was set aside to cool. Purple crystals obtained could be recrystallized from dilute iodine-free HI (yield 70%).

The salt *trans*-$[RuL^1I_2]I\cdot2H_2O$, on the other hand, could be more efficiently prepared by a direct ligand-replacement reaction by heating an aqueous mixture of *trans*-$[RuL^1Cl_2][ClO_4]$ and an excess of NaI on a steam-bath for *ca.* 1 h. The hot solution was filtered and iodine-free HI (2 cm^3) was added. On cooling, large purple leaflets slowly appeared. They were collected, washed with cold water, alcohol, and diethyl ether and dried *in vacuo* at 78 °C (yield 75%).

trans-*Bromochlorobis(ethane*-1,2-*diamine)ruthenium*(III) *Perchlorate*.—A mixture of *trans*-$[RuL^1Br_2][ClO_4]$ (0.5 g) and LiCl (1 g) in methanol (100 cm^3) was heated on a steam-bath for *ca.* 0.5 h.* Excess of $Li[ClO_4]$ was added to precipitate an orange-yellow solid which was twice recrystallized from methanol. The complex was filtered off, washed with cold methanol and diethyl ether, and dried *in vacuo* at 78 °C (yield 0.3 g).

trans-*Chlorobis(ethane*-1,2-*diamine)iodoruthenium*(III) *Perchlorate*.—This complex was prepared by heating a methanolic solution (100 cm^3) of *trans*-$[RuL^1I_2]I\cdot2H_2O$ (0.5 g) and LiCl (1 g) on a steam-bath for *ca.* 0.5 h.* Addition of excess of $Li[ClO_4]$ precipitated out a deep reddish purple solid which was twice recrystallized from methanol. This complex may also be efficiently recrystallized from dilute (0.1 mol dm^{-3}) toluene-*p*-sulphonic acid (yield 0.3 g).

trans-*Bromobis(ethane*-1,2-*diamine)iodoruthenium*(III) *Perchlorate*.—This deep reddish purple complex was prepared by essentially the same method with a similar yield as *trans*-$[RuL^1(Cl)I][ClO_4]$ except that LiBr was used instead of LiCl.

trans-*Dichloro(tetrathioether)ruthenium*(II) *Dihydrate*, *trans*-$[RuLCl_2]\cdot2H_2O$ ($L = L^8$ *or* L^9).—These two complexes were prepared by refluxing, with stirring, a mixture of $K_2[RuCl_5(OH_2)]$ (2 g) and the corresponding cyclic thioether (1.43 g) in 2-methoxyethanol (50 cm^3) for 2 d. A yellow solid gradually formed. The resulting solution was concentrated to *ca.* 15 cm^3 to increase the yield. The solid was filtered off, washed with acetone, and recrystallized from boiling dilute (0.1 mol dm^{-3}) HCl to give bright yellow crystals (yield 60%).

trans-*Dichloro*(1,4,8,11-*tetrathiacyclotetradecane*)*ruthenium*(III) *Perchlorate Monohydrate*.—This complex was prepared by adding $HClO_4$ (70%, 1 cm^3) to *trans*-$[RuL^8Cl_2]\cdot2H_2O$ dissolved in a minimum amount of hot dilute (0.1 mol dm^{-3}) HCl. The solution was heated on a steam-bath for *ca.* 2 h during which the solution turned red. It was filtered while hot and then cooled. Dark red crystals slowly appeared. They were collected, washed with a little cold water, then acetone–diethyl ether (1 : 1), and dried *in vacuo* at 78 °C (yield 70%).

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 determined with a Beckman Acta CIII spectrophotometer. Magnetic susceptibilities of solid samples were measured by the Gouy method using mercury tetrathiocyanatocobaltate(II) as the calibrant.[9] When only a small quantity of the sample was available, the magnetic susceptibilities were measured by an n.m.r. method.[10,11]

RESULTS AND DISCUSSION

The modified dropwise-addition method for the preparation of *trans*-$[RuLCl_2]^+$ is reproducible as it has been checked by several independent workers of this laboratory. The major difficulty associated with the previous method [3,4] is the presence of several ill defined by-products and, quite often, repeated recrystallization is necessary to obtain the desired complex. Since $K_2[RuCl_5(OH_2)]$ is quite insoluble in methanol,† the refluxing of a suspension of it and the stoicheiometric amount of an amine in methanol, according to the published procedure,[3,4] means that the amine ligand is effectively present in a large excess in solution which may be the reason for the complicated side reactions observed. As an illustration, two ruthenium-containing side products, a dark brown solid and a blue species, have in fact been isolated in the reaction with L^7 by allowing the final reaction solution to be evaporated to dryness and then extracting the residue with chloroform. The compounds were separated by chromatography using a Sephadex G-10 resin. Elemental analysis shows that the dark brown solid does not contain any carbon or nitrogen while the blue solid has a very high carbon content, much higher than one would have expected for one amine L^7 per ruthenium. Furthermore, the experimental carbon to nitrogen ratio in the blue species is also much greater than that expected for L^7. The intense brown colour of the former side product seems to suggest that it may be a polymeric oxo- or chloro-bridged complex of ruthenium. The outstanding feature of the i.r. spectrum of the blue solid is the presence of a strong band at 1 730 cm^{-1} which is absent in all known complexes of L^7. The fact that this band is not due to impurities has been verified by several independent preparations of the blue species and, in every case, the band at 1 730 cm^{-1} is found. This may suggest the presence of C=O or C=N groups in the compound. It has been reported [12,13] that amines co-ordinated to ruthenium(II) may be easily oxidized to imines and that

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* The optimum reaction time is best determined by continually measuring the electronic absorption spectra of samples of the reaction solution. As soon as the absorption peak of the starting complex has completely disappeared (409 nm for *trans*-$[RuL^1Br_2]^+$ and 573 nm for *trans*-$[RuL^1I_2]^+$) and a new absorption peak corresponding to the reaction product has fully developed, the reaction should be immediately quenched.

† Various solvents have been tried but methanol is still the best.

the efficiency of this process increases with pH. It is, therefore, not surprising that some sort of side redox reactions may have occurred in the previous method of preparation[3] when the amine is apparently present in a large excess. This may lead to decomposition or reorganization of the L^7 amine ligand and account for the greater carbon content in the blue compound. The normalized mass spectrum of this compound clearly shows the presence of a species of high molecular weight (*m/e* 580, *ca.* 6%). It is extremely soluble in most common solvents, such as water, acetone, chloroform, diethyl ether, and benzene, which makes the recrystallization of this compound very difficult. We have, however, not yet been able to identify the nature of both the dark brown and blue species and further investigation will be carried out.

The key step in the modified method which greatly simplifies the synthetic process probably lies in the controlled addition of the amine to the reaction mixture so that a stoicheiometric ratio of $[RuCl_5(OH_2)]^{2-}$ to amine is roughly maintained in solution. Indeed, from the u.v. study of the course of the preparative reaction between $K_2[RuCl_5(OH_2)]$ and L, a straightforward reaction with a peak at *ca.* 350 nm due to the gradual formation of *trans*-$[RuLCl_2]^+$ was followed. The same u.v. study in the previous method[3] shows the building up of additional peaks.

The general method of using silver toluene-*p*-sulphonate to remove the co-ordinated chloride and then treating the diaquo-species with an excess of the other halide is not recommended for the preparation of *trans*-$[RuLX_2]^+$ (X = Br or I) from the corresponding *trans*-$[RuLCl_2]^+$ since some ill defined dark brown side products are usually formed. Although we once prepared *trans*-$[RuL^1(OH_2)_2][ClO_4]_3$ by treating *trans*-$[RuL^1Cl_2]^+$ with silver toluene-*p*-sulphonate, the method is not always reproducible and the yield is always very poor. The preparation of this diaquo-species has not therefore been included in the Experimental section. We have noticed that[1] *trans*-$[RuLCl_2]^+$ can be quantitatively reduced electrolytically to *trans*-$[RuLCl_2]$, which then undergoes a rapid hydrolysis reaction. With this background knowledge, and by reference to the work of Isied and Taube[14] and Ford and co-workers,[15] other dihalogeno-complexes were prepared by first reducing the corresponding *trans*-$[RuLCl_2]^+$ with zinc to its ruthenium(II) analogue. Subsequent hydrolysis, and air-oxidation back to ruthenium(III), in the presence of a large excess of other halide, efficiently led to the formation of *trans*-$[RuLX_2]^+$ (X = Br or I). However, for L^1 complexes, since the acid hydrolysis of *trans*-$[RuL^1Cl_2]^+$ occurs the fastest of all analogous dichloro-complexes in the present investigation, the direct replacement of the co-ordinated chloride by X^- may also lead directly to the formation of *trans*-$[RuL^1X_2]^+$. For the preparation of *trans*-$[RuL^1(I)X]^+$ (X = Cl or Br), the use of *trans*-$[RuL^1I_2]^+$ as the starting material rather than *trans*-$[RuL^1X_2]^+$ (X = Cl or Br) is important since I^- is a much better *trans*-labilizing ligand than bromide or chloride[16] in octahedral ruthenium complexes. The reaction between *trans*-$[RuL^1X_2]^+$ (X = Cl or Br) and a stoicheiometric amount of iodide would have led to the formation of the di-iodo-complex instead.

All the new complexes are highly coloured and give well formed crystals which appear to be stable indefinitely in the solid state. The isomeric purity of each complex was confirmed by the observation that the electronic absorption spectrum of the complex was unaffected by repeated recrystallization. In some cases, this was further confirmed by absorbing the complexes on a Dowex 50W-X8 (20—50 mesh) cation exchanger in the acid form. Only a single band was developed which could be eluted out.

The magnetic moments and molar conductivities of these complexes (Table 2) confirm that they are low-spin monomeric species. Assuming a D_{4h} microsymmetry of the dihalogeno-complexes (or C_{4v} for mixed halogeno-complexes) with the *z* axis lying along the X–Ru–X axis, there are two possible orderings of the valence *d* orbitals depending on the relative energies of the essentially non-bonding d_{xy} orbital and the π-antibonding d_{xz} and d_{yz} pair (Figure 1). Unfortunately, our observed magnetic moments cannot differentiate between these two alternatives and hence we cannot assign the proper ground state, whether ^2B_g or ^2E_g, to these ruthenium(III) complexes. The two ruthenium(II) complexes will have, unquestionably, the $^1A_{1g}$ ground state. For the corresponding *trans*-$[FeL^7X_2]^+$ (X = Cl or NCS) complexes, e.s.r. studies[17] have shown that the d_{xy} orbital is lower in energy than the d_{xz} and d_{yz} pair. Our e.s.r. study on the ruthenium(III) complexes is now in progress[18] and we postpone its discussion to a later paper.

TABLE 2

Magnetic moments ($\mu_{eff.}$) and molar conductivities (Λ) of some *trans*-ruthenium complexes

Complex	$\mu_{eff.}$ [a] / B.M.	Λ [b] / Ω^{-1} cm^2 mol^{-1}
$[RuL^1Cl_2][ClO_4]$	2.23 (295)	93
$[RuL^1Br_2][ClO_4]$	2.20 (293)	101
$[RuL^1I_2]I\cdot 2H_2O$	2.11 (293)	108
$[RuL^1(Cl)Br][ClO_4]$	2.20 (294)	104
$[RuL^1(Cl)I][ClO_4]$	2.15 (294)	115
$[RuL^1(Br)I][ClO_4]$	2.16 (294)	113
$[RuL^2Cl_2][ClO_4]$	2.20 (291)	100
$[RuL^2Br_2][ClO_4]$	2.14 (291)	104
$[RuL^3Cl_2][ClO_4]$	2.23 (291)	100
$[RuL^4Cl_2][ClO_4]$	2.12 (295)	97
$[RuL^4Br_2][ClO_4]$	2.18 (291)	98
$[RuL^4I_2]I$	2.10 (295)	*c*
$[RuL^5Cl_2][ClO_4]$	2.19 (293)	104
$[RuL^6Cl_2][ClO_4]$	2.21 (293)	97
$[RuL^7Cl_2]Cl$	2.10 (295)	110
$[RuL^7Br_2]Br$	2.17 (291)	104
$[RuL^8Cl_2]\cdot 2H_2O$	0 (308) [d]	13.8 [e]
$[RuL^8Cl_2][ClO_4]\cdot H_2O$	2.10 (308)	*c*
$[RuL^9Cl_2]\cdot 2H_2O$	0 (308) [d]	5.5 [e]

[a] By Gouy method except as indicated; temperature (K) of measurement is given in parentheses. 1 B.M. = 9.274×10^{-24} A m^2. [b] In deionized water at 18 °C except as indicated. [c] The experimental reading gradually increases, indicating that hydrolysis is taking place. [d] By the n.m.r. method in acetonitrile. [e] In acetonitrile at 22 °C.

The assignment of a *trans* configuration to these com-

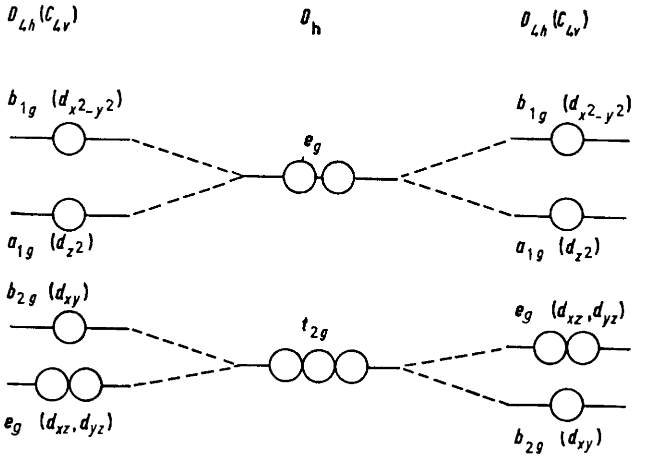

FIGURE 1 Two possible orderings of valence *d* orbitals of *trans*-$[\mathrm{RuL(X)Y}]^{n+}$ of D_{4h} (X = Y) or C_{4v} (X ≠ Y) symmetry containing a relatively weak average axial-ligand field

plexes is made on the basis of both i.r. (including far-i.r.) and electronic absorption spectroscopy. The i.r. spectra of these complexes in the 790—930 $\mathrm{cm^{-1}}$ region of interest together with those bands assignable to the ν(Ru–X) stretch are collected in Table 3. For the $\mathrm{L^1}$, $\mathrm{L^2}$, $\mathrm{L^4}$, and $\mathrm{L^7}$ complexes, a comparison of the far-i.r. spectra of the dichloro-complexes with their corresponding dibromo-, or even with their di-iodo-, complexes enabled the ν(Ru–X) stretching frequencies to be determined (Figure 2). In all cases, only one strong band was observed which unambiguously showed that these dichloro- and dibromo-complexes have a *trans* configuration. The ν(Ru–I) stretching frequencies of di-iodo-complexes occurred well below our instrumental limit of 200 $\mathrm{cm^{-1}}$ and hence could not be determined, but their configuration can be inferred from other spectroscopic information. For $\mathrm{L^6}$, $\mathrm{L^8}$, and $\mathrm{L^9}$ complexes, although their dibromo-complexes are not available for comparison, a study of their far-i.r. spectra showed that there was only one intense band in the background of a number of medium and weak bands. For the $\mathrm{L^6}$ and $\mathrm{L^8}$ ruthenium(III) complexes, the position of this intense band at 322 and 305 $\mathrm{cm^{-1}}$ respectively is in the same frequency range as that of the $\nu(\mathrm{Ru^{III}-Cl})$ stretch of analogous $\mathrm{L^1}$, $\mathrm{L^2}$, $\mathrm{L^4}$, and $\mathrm{L^7}$ dichloro-complexes. Clearly, the intense band can be assigned a $\nu(\mathrm{Ru^{III}-Cl})$ stretch and hence the complexes have a *trans* configuration. As for the two $\mathrm{L^8}$ and $\mathrm{L^9}$ ruthenium(II) complexes, the intense band at a slightly lower frequency (250 and 240 $\mathrm{cm^{-1}}$ respectively) is also consistent with a $\nu(\mathrm{Ru^{II}-Cl})$ stretch. The presence of only one such band also suggests a *trans* configuration for these complexes. In fact, a comparison of the far-i.r.

TABLE 3

Infrared spectra in the 790—930 and 200—400 $\mathrm{cm^{-1}}$ regions [a] of some *trans*- and *cis*-ruthenium complexes

Complex	Absorption bands ($\mathrm{cm^{-1}}$)	
	CH$_2$ and/or NH vibration	Ru–X stretch
trans-$[\mathrm{RuL^1Cl_2}][\mathrm{ClO_4}]$	890m, 881w (sh)	330s
trans-$[\mathrm{RuL^1Br_2}][\mathrm{ClO_4}]$	891m, 880w (sh)	220s
trans-$[\mathrm{RuL^1I_2}]\mathrm{I\cdot 2H_2O}$	875m	*b*
trans-$[\mathrm{RuL^1(Cl)Br}][\mathrm{ClO_4}]$	885m	325s, br, 210m
trans-$[\mathrm{RuL^1(Cl)I}][\mathrm{ClO_4}]$	882m	310s
trans-$[\mathrm{RuL^1(Br)I}][\mathrm{ClO_4}]$	880m	205s
cis-$[\mathrm{RuL^1Cl_2}]\mathrm{Cl\cdot H_2O}$ [c]	886m, 867m	322w (sh), 311m, 273s
trans-$[\mathrm{RuL^2Cl_2}][\mathrm{ClO_4}]$	890m, 882m, 850w	332s
trans-$[\mathrm{RuL^2Br_2}][\mathrm{ClO_4}]$	890m, 882m, 850w	242s
trans-$[\mathrm{RuL^3Cl_2}][\mathrm{ClO_4}]$	860s, 822s	*d*
trans-$[\mathrm{RuL^4Cl_2}][\mathrm{ClO_4}]$	892s, 876s, 806m	320s
trans-$[\mathrm{RuL^4Br_2}][\mathrm{ClO_4}]$	890s, 870s, 800m	240s
trans-$[\mathrm{RuL^4I_2}]\mathrm{I}$	881s, 870s, 800m	*b*
trans-$[\mathrm{RuL^5Cl_2}][\mathrm{ClO_4}]$	900s, br, 872s, 860s	*d*
trans-$[\mathrm{RuL^6Cl_2}][\mathrm{ClO_4}]$	912s, 894s, 850w	322s
trans-$[\mathrm{RuL^7Cl_2}]\mathrm{Cl}$	898s, 888s, 805s	322s
trans-$[\mathrm{RuL^7Br_2}]\mathrm{Br}$	883s, 872s, 795s	220s
trans-$[\mathrm{RuL^8Cl_2}]\mathrm{\cdot 2H_2O}$	930m, 925m, 910m, 860s, 850m, 845m (sh), 818m	250s
trans-$[\mathrm{RuL^8Cl_2}][\mathrm{ClO_4}]\mathrm{\cdot H_2O}$	925m, 905m, 860s, 850s (sh), 842m, 818m	305s
trans-$[\mathrm{RuL^9Cl_2}]\mathrm{\cdot 2H_2O}$	930w, 925w (sh), 895w, 860s, 845m (sh), 815w	240s

[a] Bands other than ν(Ru–X) are not given in this Table; s = strong, m = medium, w = weak, sh = shoulder, and br = broad. [b] Occurs well below the instrument limit of 200 $\mathrm{cm^{-1}}$. [c] J. A. Broomhead and L. A. P. Kane-Maguire, *J. Chem. Soc.* (*A*), 1967, 546. [d] Assignment of ν(Ru–Cl) is not certain for this complex.

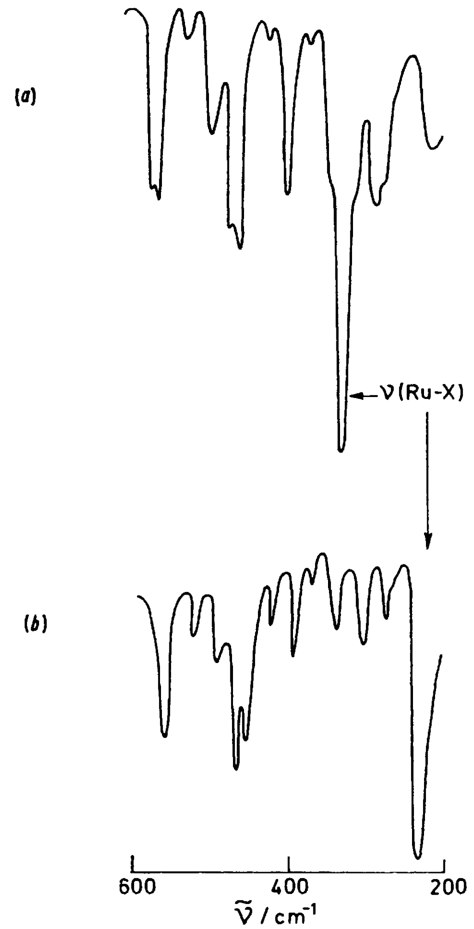

FIGURE 2 Far-i.r. spectra in the 200—600 $\mathrm{cm^{-1}}$ region of *trans*-(*R*,*S*)-$[\mathrm{RuL^4X_2}][\mathrm{ClO_4}]$ [X = Cl (*a*) or Br (*b*)]

spectra of $[RuL^8Cl_2]\cdot 2H_2O$ and $[RuL^8Cl_2][ClO_4]\cdot H_2O$ confirms the above assignment of the $\nu(Ru^{II}–Cl)$ and $\nu(Ru^{III}–Cl)$ bands, as these two spectra only differ in the position of this intense band. In the absence of the corresponding dibromo-complexes for comparison, however, a study of the far-i.r. spectra of $[RuLCl_2][ClO_4]$ ($L = L^3$ and L^5) alone cannot single out the $\nu(Ru–Cl)$ stretch. The assignment of geometrical configuration to these two complexes will depend on other information discussed below. As for the mixed halogeno-complexes, a comparison of the individual far-i.r. spectra with those of the dihalogeno-complexes enabled the appropriate $\nu(Ru–X)$ bands to be assigned. However, this information alone does not help in deciding the geometrical configuration of the mixed halogeno-complexes, which can be determined by a study of the i.r. spectra. For L^8 and L^9 complexes we have not been able to assign the $\nu(Ru–S)$ stretch with confidence.

The i.r. spectra in the 790—930 cm^{-1} region are also very useful for the identification of geometrical isomerism in these complexes. For L^1 complexes, consistent variations have been found in the CH_2 rocking (870—900 cm^{-1}) mode, where splitting occurred for the *cis* but not for the *trans* isomers.[19] This criterion is also very useful here, especially for the di-iodo- and mixed halogeno-complexes where far-i.r. spectroscopy (limited by our instrument to 200 cm^{-1}) is not particularly useful. As shown in Table 3, all the L^1 complexes prepared here have a *trans* configuration. Although a weak shoulder (splitting) appears for the dichloro- and dibromo-complexes, the assignment of a *trans* configuration to these two complexes has been confirmed by the far-i.r. spectroscopy and by a comparison of other physical and chemical properties with their corresponding *cis* isomers.[3-5] The assignment of a *trans* configuration to all L^4 and L^7 complexes is also very clear-cut since a doublet occurs near 890 cm^{-1} and a singlet near 800 cm^{-1}.[3,4,20,21] The i.r. spectra of other relevant complexes have not been discussed before and, in the absence of the corresponding *cis* isomers for comparison, it is difficult to draw any conclusion concerning their usefulness in the differentiation of geometrical isomerism. A close look at the i.r. spectra of L^2, L^5, and L^6 complexes shows a high degree of similarity among them. These complexes are essentially dominated by six-membered chelate rings involving the trimethylene chains. The similarity of their i.r. spectra in this region seems to suggest that they all have the same geometrical configuration, which, according to the far-i.r. spectrum of the L^2 and L^6 dichloro-complexes, means that they all assume a *trans* configuration. This conclusion is supported by the electronic absorption spectra which will be discussed later. The three thioether complexes also have very similar i.r. spectra in this region, endorsing their common geometrical configuration. The case of *trans*-$[RuL^3Cl_2][ClO_4]$ is rather unusual. Neither the i.r. in this region nor the far-i.r. spectra are useful in deciding the geometrical configuration. The only useful information that can be drawn from the i.r. spectrum is the presence of only one sharp intense band at 3 240 cm^{-1} arising from the secondary amine vibration. This strongly indicates a *trans* configuration, which, once again, is supported by the electronic absorption spectrum.

The electronic absorption spectra of the ruthenium(III) complexes (Table 4) are dominated by the intense ligand-to-metal charge-transfer transitions, as confirmed by the gradual red shift of the lowest-energy $\lambda_{max.}$ from chloro- through bromo- to iodo-complexes. Since we have not been able to decide the ground state of these ruthenium(III) complexes (^2B_g or ^2E_g), we shall assume, for simplicity, that all these transitions are residing on the metal t_{2g} type orbitals of octahedral parentage. For the tetramine dihalogeno-complexes, $\pi_{Cl}\rightarrow t_{2g}$ transitions occur near 350 nm, $\pi_{Br}\rightarrow t_{2g}$ near 420 nm, and $\pi_{I}\rightarrow t_{2g}$ around 580 nm. A comparison of mixed halogeno-complexes *trans*-$[RuL^1(X)Y]^+$ with *trans*-$[RuL^1X_2]^+$ (X = Cl, Br, or I) reveals that the lowest-energy charge-transfer transitions in the former lie between those of the corresponding pairs of dihalogeno-complexes. This strongly suggests that these transitions are essentially combination modes in the mixed halogeno-complexes. As an illustration, $\lambda_{max.}$ of *trans*-$[RuL^1(Cl)Br]^+$ (387 nm) lies between those of *trans*-$[RuL^1Cl_2]^+$ (343 nm) and *trans*-$[RuL^1Br_2]^+$ (409 nm in HBr medium). This suggests that the band at 387 nm of *trans*-$[RuL^1(Cl)Br]^+$ is essentially a $(\pi_{Cl},\pi_{Br})\rightarrow t_{2g}$ transition. Although the positions of these transitions are solvent dependent, as illustrated by the two different values of $\lambda_{max.}$ for *trans*-$[RuL^1Br_2]^+$ in two different solvents, the difference is not large enough to upset the above conclusion. Within the same series of *trans*-dichlorotetramineruthenium(III) complexes, $\lambda_{max.}$ gradually increases with L in the order: $L^1 < L^2 < L^4 < L^5 < L^3 < L^6 < L^7$. With the exception of L^3 this is the order of increasing chelate ring size about the central metal ion. For other series of *trans*-dibromo- and *trans*-iodo-complexes, although there are fewer members in each series for comparison, $\lambda_{max.}$ does increase with the same order of L. Moving to the tetrathioether complexes, a comparison of the spectra of *trans*-$[RuL^8Cl_2]^+$ and *trans*-$[RuL^8Cl_2]$ (*i.e.* Ru^{III} against Ru^{II}) shows quite clearly that the band of the former at 560 nm must be a ligand-to-metal charge-transfer transition. A further comparison of the spectra of *trans*-$[RuL^8Cl_2]^+$ with those of *trans*-$[RuLCl_2]^+$ (L = tetramines L^1 to L^7) suggests that the band at 560 nm should be assigned to a $\pi_s\rightarrow t_{2g}$ transition. As for the two remaining ruthenium(II) complexes, *trans*-$[RuLCl_2]\cdot 2H_2O$ ($L = L^8$ or L^9), the intensity of the lowest-energy band suggests that it is a ligand-field transition, $^1A_{1g}\rightarrow {}^1T_{1g}$ (again, of octahedral parentage). Included in Table 4 are the electronic spectra of three closely related *trans*-bis(bidentate)(tetrathioether) ruthenium(II) complexes for comparison. As for the use of electronic absorption spectroscopy to differentiate between geometrical isomers of these ruthenium(III) complexes, it is quite clear from Table 4 that this is not a particularly useful method. For example, the electronic spectra of *cis*- and *trans*-$[RuL^1Cl_2]^+$ are very similar as regards positions and number of bands, although the lowest-energy $\pi_{Cl} \rightarrow t_{2g}$ transition for the *trans* isomer is much more intense and slightly higher in energy. The same trend is slightly more magnified for the pair *cis*- and *trans*-$[RuL^1Br_2]^+$. Therefore, given the spectrum of one single complex alone, it would be rather difficult to assign with confidence its geometrical configuration. However, when the spectra of an extensive series of analogous complexes are available, it is still a useful method, which, from the systematic variation of $\lambda_{max.}$ with L and its generally high intensity, gives strong support to the assignment of a common geometrical (*trans*) configuration to these complexes.

TABLE 4

Visible and u.v. absorption spectra of some ruthenium tetramine and tetrathioether complexes

Complex	Solvent [a]	$\lambda_{max.}$/nm [b]
cis-$[RuL^1Cl_2]Cl\cdot H_2O$ [c]	HCl	354 (1 750), 314 (1 420), 269 (900)
trans-$[RuL^1Cl_2][ClO_4]$ [d]	HCl	343 (3 850), 292br (sh) (800), 272br (sh) (900)
trans-$[RuL^1Cl_2]Cl\cdot 0.5H_2O$ [e]	HCl	342 (4 080), 295 (sh) (745), 268 (sh) (810)
trans-$[RuL^2Cl_2][ClO_4]$	HCl	346 (3 460), 291 (1 380)
trans-$[RuL^3Cl_2][ClO_4]$	HCl	352 (2 830), 312 (1 450)
trans-$[RuL^4Cl_2][ClO_4]$	HCl	349 (3 430), 297 (1 160)
trans-$[RuL^5Cl_2][ClO_4]$	HCl	351 (2 560), 302 (1 230)
trans-$[RuL^6Cl_2][ClO_4]$	HCl	353 (2 610), 305 (1 450)
trans-$[RuL^7Cl_2]Cl$	HCl	357 (2 260), 312 (1 250)
cis-$[RuL^1Br_2]Br\cdot H_2O$ [c]	HBr	445 (1 530), 380 (1 510)
trans-$[RuL^1Br_2]Br$ [e]	HBr	409 (4 680), 382 (770)
trans-$[RuL^1Br_2][ClO_4]$	CH_3OH	416 (5 140), 395 (sh) (3 110), 348 (898), 250 (sh) (2 660)
trans-$[RuL^2Br_2][ClO_4]$	CH_3OH	418 (4 970), *ca.* 400br (sh) (2 490), 352 (950), 250 (sh) (2 580)
trans-$[RuL^4Br_2][ClO_4]$	CH_3OH	423 (4 890), 406 (sh) (2 610), 352 (1 000), 250 (sh) (2 300)
trans-$[RuL^7Br_2]Br$	CH_3OH	436 (4 530), 410 (sh) (2 140), 358br (876), 315br (sh), (390), 255 (sh) (2 060)
trans-$[RuL^1I_2]I\cdot 2H_2O$	CH_3OH	573 (7 070), 540 (sh) (3 470), *ca.* 490br (sh) (680), 388 (740), 308 (9 800)
trans-$[RuL^4I_2]I$	CH_3OH	588 (4 970), 550 (sh) (2 000), *ca.* 490br (sh) (750), 394 (484), 310 (6 680)
trans-$[RuL^1(Cl)Br][ClO_4]$	HCl	387 (2 100), 344 (1 800), 296br (sh) (580)
trans-$[RuL^1(I)Br][ClO_4]$	CH_3OH	527 (2 890), *ca.* 490 (sh) (1 580), 412br (sh) (1 350), 396br (sh) (1 430), 376 (sh) (1 080), 382 (4 300)
trans-$[RuL^1(I)Cl][ClO_4]$	HCl	520 (2 040), *ca.* 470br (sh) (1 160), *ca.* 330 (sh) (1 280), *ca.* 306br (sh) (1 800), 270 (3 240)
cis-$[RuL^1(I)Cl]I\cdot H_2O$ [c]	H_2O	640 (670), 524 (950), 427 (490), 375 (sh) (670)
trans-$[RuL^8Cl_2][ClO_4]\cdot H_2O$	HCl	560 (932), *ca.* 485br (sh) (740), 424 (1 350), *ca.* 350 (sh) (1 620), 323 (2 050)
trans-$[RuL^8Cl_2]\cdot 2H_2O$	CH_3CN	*ca.* 430br (sh) (125), 360 (1 010), 298 (1 090), 246 (sh) (3 550)
trans-$[RuL^9Cl_2]\cdot 2H_2O$	CH_3CN	*ca.* 440br (sh) (72), 362 (984), 284 (sh) (1 660)
trans-$[RuL^{10}Cl_2]$ [f]	C_2H_5OH	476 (48), 357 (138), 270 (?)
trans-$[RuL^{11}Cl_2]$ [f]	C_2H_5OH	476 (46), 357 (131), 270 (?)
trans-$[RuL^{12}Cl_2]$ [f]	$CHCl_3$	482 (175), 416 (320), 310 (?)

[a] 0.1—1.0 mol dm^{-3} HCl (or HBr). [b] Molar absorption coefficients ($\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$) are given in parentheses; abbreviations: br, broad; sh, shoulder. [c] J. A. Broomhead and L. A. P. Kane-Maguire, *J. Chem. Soc.* (*A*), 1967, 546. [d] Ref. 3. [e] Ref. 5. [f] J. Chatt, G. Leigh, and A. P. Storace, *J. Chem. Soc.* (*A*), 1971, 1380; molar absorptions of the bands at 270 and 310 nm were not reported. Abbreviations: $L^{10} = (Pr^nSCH_2CH_2SPr^n)_2$; $L^{11} = (EtSCH_2CH_2SEt)_2$; and $L^{12} = (PhSCH_2CH_2SPh)_2$.

Finally, it should be pointed out that the assignment of a *trans* configuration does not fully characterize the L^3, L^4, L^5, L^6, and L^7 complexes because they contain two (for L^4, L^5, and L^6) or four (for L^3 and L^7) chiral nitrogen centres. The dichloro-complexes of L^4 and L^7 have been fully characterized [4,22,23] to have the *R,S* and *R,S,S,R* configurations respectively. Since all derivatives of L^4 and L^7 complexes are obtained from the corresponding dichloro-complexes under acidic conditions and their i.r. spectra are similar it is quite safe to conclude that all L^4 and L^7 complexes reported here have the same configuration as their dichloro-analogues. The configuration of *trans*-$[RuLCl_2]^+$ ($L = L^3$, L^5, or L^6), however, cannot be decided from the present study. These complexes are paramagnetic and we cannot use the n.m.r. technique to help solve the problem, which, therefore, must await a future investigation.

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