Structural and Mechanistic Studies of Co-ordination Compounds. Part 29.[1] Synthesis and Characterization of Some *cis*-Macrocyclic Secondary Amine Complexes of Ruthenium

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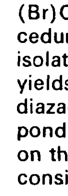
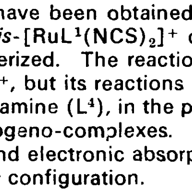
Under suitably controlled conditions, the reaction between trioxalatoruthenate(III), $[Ru(O_4C_2)_3]^{3-}$, and 1,4,8,11-tetra-azacyclotetradecane (L^1) in the presence of an acid HX leads to the formation of the corresponding *cis*-$[RuL^1X_2]^+$ (X = Cl or Br) in *ca.* 50% yield. Other complexes of the type *cis*-$[RuL^1(X)Y]^+$ [(X)Y = I_2, $(NCS)_2$, (Br)Cl, or oxalate] have been obtained from either the dichloro- or the dibromo-complex by metathetical procedures. The ion *cis*-$[RuL^1(NCS)_2]^+$ can easily be reduced and the product *cis*-$[RuL^1(NCS)_2]\cdot H_2O$ has been isolated and characterized. The reaction of $[Ru(O_4C_2)_3]^{3-}$ with 1,4,8,12-tetra-azacyclopentadecane (L^2) in HBr yields *cis*-$[RuL^2Br_2]^+$, but its reactions with open-chain tetramines, 3,7-diazanonane-1,9-diamine (L^3) and 4,7-diazadecane-1,10-diamine (L^4), in the presence of HX (X = Cl or Br) only resulted in the formation of the corresponding *trans*-dihalogeno-complexes. The assignment of a *cis* configuration to these complexes has been made on the basis of i.r. and electronic absorption spectroscopy. The ^1H n.m.r. spectrum of *cis*-$[RuL^1(NCS)_2]\cdot H_2O$ is consistent with a *cis* configuration.

As part of our programme to extend the kinetic and mechanistic studies of hydrolysis reactions from cobalt amine complexes to other metal systems, we have reported the synthesis [2,3] of an extensive series of ruthenium(III) complexes of the type *trans*-$[RuL(X)Y]^{n+}$ where L represents either two bidentate or one quadridentate amine and X and Y are two unidentate ligands. We have also studied the acid and base hydrolysis of some *trans*-dichloro-complexes.[4,5]

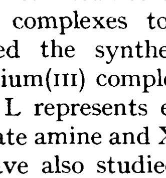
In an attempt to understand the *cis* and *trans* effects of macrocyclic amine ligands on the reactivities of these ruthenium(III) complexes, we report here the synthesis of some *cis*-macrocyclic amine complexes: *cis*-$[RuL^1(X)Y]^+$ [L^1 = 1,4,8,11-tetra-azacyclotetradecane,



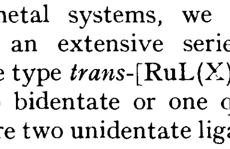
L^1



L^2



L^3



L^4

(X)Y = Cl_2, Br_2, I_2, (Br)Cl, $(NCS)_2$, or oxalate], *cis*-$[RuL^2Br_2]^+$ (L^2 = 1,4,8,12-tetra-azacyclopentadecane), and *cis*-$[RuL^1(NCS)_2]\cdot H_2O$. At the final stage of characterization of these new complexes, the synthesis of *cis*-$[RuL^1Cl_2]^+$ was reported by Isied.[6] He followed our previous method [2] of preparing *trans*-$[RuL^1Cl_2]^+$ and reported that he had also isolated the *cis* isomer as a by-product. However, the i.r. and electronic absorption spectra of his complex are quite different from those of our *cis*-$[RuL^1Cl_2]Cl$ reported herein. References are made to other well characterized *cis*- and *trans*-$[ML^1Cl_2]^+$ [M = Co^{III}, Cr^{III}, or Fe^{III}] in a comparative study of the nature of our *cis*-$[RuL^1Cl_2]Cl$ and Isied's complex.

EXPERIMENTAL

Synthesis of Complexes.—*cis* Complexes of L^1 and L^2 were synthesized from trioxalatoruthenate(III), $[Ru(O_4C_2)_3]^{3-}$. The salt $K_3[Ru(O_4C_2)_3]\cdot 4H_2O$ was first reported by Charonnet,[7,8] but it was found more convenient and efficient to generate the complex anion in solution and use it whilst fresh for subsequent preparations.

Potassium trioxalatoruthenate(III) was prepared by refluxing an aqueous solution (25 cm^3) of $K_2[RuCl_5(OH_2)]$ (2 g) and oxalic acid (1.6 g) for 2.5 h. Solid $Na_2[CO_3]$ was added continually in small quantities until the pH of the solution reached *ca.* 7 and the evolution of carbon dioxide subsided. After heating on a steam-bath for another 20 min, the resulting olive-green solution was ready for use in the preparation of the following complexes, without the need for isolation of $K_3[Ru(O_4C_2)_3]$. Alternatively, $RuBr_3$ could be used as the starting material instead of $K_2[RuCl_5(OH_2)]$. In this case the reaction time should be longer (*ca.* 4 h).

cis-*Dichloro*(1,4,8,11-*tetra-azacyclotetradecane*)*ruthenium*(III) *chloride.* A partially neutralized aqueous solution of L^1 was first prepared by adding dilute HCl to an aqueous solution of L^1 (1 g in 25 cm^3) until the pH of the solution was *ca.* 6.5. This solution was slowly added to a hot freshly prepared solution of $[Ru(O_4C_2)_3]^{3-}$ and the pH was adjusted to *ca.* 7 using either $Na_2[CO_3]$ or HCl as appropriate. The resulting solution was refluxed for 3 h during which the colour gradually became reddish brown. Concentrated HCl (10 cm^3) was added and the solution was refluxed for another 30 min. To the hot filtered solution, concentrated HCl (10 cm^3) was added and the solution was concentrated down to *ca.* 30 cm^3. On cooling, yellow crystals were slowly deposited. They were collected and recrystallized from a minimum volume of boiling HCl (1 mol dm^{-3}). Concentrated HCl (8 cm^3) was then added to the filtered hot solution. On cooling, bright yellow crystals were slowly deposited. These were collected, washed with a small quantity of ice-cold water, ethanol–diethyl ether, then diethyl ether, and dried *in vacuo* at 78 °C (yield 50%) (Found: C, 29.4; H, 5.8; Cl, 26.3; N, 13.5. Calc. for $C_{10}H_{24}Cl_3N_4Ru$: C, 29.4; H, 5.9; Cl, 26.1; N, 13.7%).

cis-*Dibromo*(1,4,8,11-*tetra-azacyclotetradecane*)*ruthenium*(III) *bromide hemihydrate*. This complex was similarly prepared with similar yield to its dichloro-analogue except that HBr was used instead of HCl.

Alternatively, it could be prepared from *cis*-$[RuL^1Cl_2]Cl$. A hot solution (25 cm^3) of *cis*-$[RuL^1Cl_2]Cl$ (0.5 g) in toluene-*p*-sulphonic acid (0.1 mol cm^{-3}) was treated with concentrated HBr (5 cm^3) and then heated on a steam-bath for 1 h. A red solid was gradually deposited. It was collected and recrystallized from a minimum volume of hot HBr (0.1 mol dm^{-3}). Addition of concentrated HBr (10 cm^3), followed by heating on a steam-bath for 15 min, yielded bright red crystals. These were collected, washed with a small quantity of ice-cold water, ethanol–diethyl ether, then diethyl ether, and finally dried *in vacuo* at 78 °C (yield 80%) (Found: C, 22.1; H, 4.8; Br, 43.7; N, 10.5. Calc. for $C_{10}H_{25}Br_3N_4O_{0.5}Ru$: C, 21.9; H, 4.6; Br, 43.6; N, 10.2%).

cis-*Di-iodo*(1,4,8,11-*tetra-azacyclotetradecane*)*ruthenium*(III) *iodide monohydrate*. A filtered saturated solution of NaI (5 cm^3) was added to a hot solution (30 cm^3) of *cis*-$[RuL^1X_2]X$ (X = Cl or Br, 0.5 g) in toluene-*p*-sulphonic acid (2 mol dm^{-3}) and the resulting solution was heated on a steam-bath with swirling for 20 min. A violet-red solid was gradually deposited. This was filtered off and recrystallized from a minimum volume of hot toluene-*p*-sulphonic acid (2 mol dm^{-3}). The resulting hot blue solution was treated with an excess of NaI, followed by heating on a steam-bath for 10 min. Violet-red crystals were gradually deposited. The recrystallization process may be repeated, if necessary, to ensure the purity of the complex. The crystals were filtered off, washed with a small quantity of ice-cold water, ethanol–diethyl ether, then with diethyl ether, and dried *in vacuo* at 78 °C (yield 70%) (Found: C, 17.1; H, 3.7; I, 54.3; N, 8.2. Calc. for $C_{10}H_{26}I_3N_4ORu$: C, 17.1; H, 3.7; I, 54.4; N, 8.0%).

cis-*Bromochloro*(1,4,8,11-*tetra-azacyclotetradecane*)*ruthenium*(III) *bromide*. The salt *cis*-$[RuL^1Cl_2]Cl$ (0.5 g), suspended in a warm solution (70 °C, 20 cm^3) of toluene-*p*-sulphonic acid (1 mol dm^{-3}), was treated with concentrated HBr (6 cm^3). The solution was heated on a steam-bath with swirling and the reaction time was monitored by periodically scanning the u.v. spectrum of the solution. The reaction was quenched immediately when an absorption peak at *ca.* 500 nm began to develop. This usually took *ca.* 20 min. During the course of the reaction small quantities of the desired orange-red crystals may be deposited. Concentrated HBr (5 cm^3) was then added to the solution to crystallize out more of the product which was collected, washed with several portions of ice-cold water (5 cm^3), ethanol–diethyl ether, then with diethyl ether, and dried *in vacuo* at 78 °C (yield 50%) (Found: C, 24.4; H, 5.0; Br, 32.2; Cl, 7.3; N, 11.5. Calc. for $C_{10}H_{24}Br_2ClN_4Ru$: C, 24.2; H, 4.8; Br, 32.2; Cl, 7.2; N, 11.3%).

cis-*Oxalato*(1,4,8,11-*tetra-azacyclotetradecane*)*ruthenium*(III) *perchlorate*. An aqueous solution (25 cm^3) of *cis*-$[RuL^1Cl_2]Cl$ and an excess of oxalic acid (5 g) were refluxed for 2 h. The solution was filtered whilst hot and an excess of $Na[ClO_4]$ was added. On cooling, yellow crystals were slowly deposited. These were filtered off, washed with a small quantity of ice-cold water, ethanol–diethyl ether, then with diethyl ether, and dried *in vacuo* at 78 °C (yield 70%) (Found: C, 29.1; H, 4.8; Cl, 7.6; N, 11.5. Calc. for $C_{12}H_{24}ClN_4O_8Ru$: C, 29.5; H, 4.9; Cl, 7.3; N, 11.5%).

cis-*Di-isothiocyanato*(1,4,8,11-*tetra-azacyclotetradecane*)-*ruthenium*(III) *perchlorate*. The salt Na[NCS] (0.5 g) (**CAUTION:** excess should be avoided) was added to a hot solution (*ca.* 70 °C, 30 cm^3) of *cis*-$[RuL^1Br_2]Br$ in toluene-*p*-sulphonic acid (2 mol dm^{-3}) and the resulting solution was heated on a hot water-bath (*ca.* 70 °C) for 20 min. An excess of $Na[ClO_4]$ was added to the final hot filtered solution. On standing for several hours a microcrystalline deep violet-red solid was slowly deposited. It was collected, washed with a small quantity of ice-cold water, ethanol–diethyl ether, then with diethyl ether, and dried *in vacuo* at 78 °C (yield 75%) (Found: C, 27.9; H, 4.8; N, 16.5; S, 12.6. Calc. for $C_{12}H_{24}ClN_6O_4RuS$: C, 27.9; H, 4.7; N, 16.3; S, 12.4%).

cis-*Di-isothiocyanato*(1,4,8,11-*tetra-azacyclotetradecane*)-*ruthenium*(II) *monohydrate*. An excess of Na[NCS] was added to a hot aqueous solution (*ca.* 70 °C, 30 cm^3) of *cis*-$[RuL^1Cl_2]Cl$ (0.5 g) and the resulting solution was heated on a steam-bath for 30 min. An orange-red solid was gradually deposited. The solution was cooled to room temperature and the product was collected, washed with hot water, ethanol–diethyl ether, then with diethyl ether, and dried *in vacuo* at 78 °C (yield 60%) (Found: C, 33.1; H, 5.8; N, 19.1; S, 14.9. Calc. for $C_{12}H_{26}N_6ORuS_2$: C, 33.1; H, 6.0; N, 19.3; S, 14.7%).

cis-*Dibromo*(1,4,8,12-*tetra-azacyclopentadecane*)*ruthenium*(III) *bromide*. The method of preparation is very similar to that of *cis*-$[RuL^1Br_2]Br$. A partially neutralized solution of L^2 (1 g in 25 cm^3) was added with stirring to a hot freshly prepared solution of $[Ru(O_4C_2)_3]^{3-}$ and the pH of the final solution was adjusted to *ca.* 7 (*should never be less than* 6.5!) using either $Na_2[CO_3]$ or HCl as appropriate. The solution was heated on a steam-bath for *ca.* 3 h during which the pH of the solution was periodically checked and maintained at *ca.* 7. Concentrated HBr (5 cm^3) was added and the solution was heated for another 15 min. The solution was filtered whilst hot when some dark solid may appear. Any dark residue was filtered off, washed with boiling HBr (10 cm^3, 0.5 mol dm^{-3}), and the washing was combined with the filtrate. Concentrated HBr (15 cm^3) was added and the resulting solution was heated on a steam-bath for another hour before it was concentrated down to *ca.* 25 cm^3. On cooling, a deep reddish brown solid was deposited. It was filtered off and recrystallized from a minimum volume of hot HBr (*ca.* 20 cm^3, 1 mol dm^{-3}). The solution was filtered whilst hot and was treated with concentrated HBr (10 cm^3). On cooling, red *cis*-$[RuL^2Br_2]Br$ was deposited. This was collected, washed with a small quantity of ice-cold water, ethanol-diethyl ether, then with diethyl ether, and dried *in vacuo* at 78 °C (yield 25%) (Found: C, 23.6; H, 4.7; Br, 43.0; N, 10.0. Calc. for $C_{11}H_{26}Br_3N_4Ru$: C, 23.8; H, 4.7; Br, 43.2; N, 10.1%).

trans-*Dichloro*(*tetramine*)*ruthenium*(III) *perchlorate*, *trans*-$[RuLCl_2][ClO_4]$ [L = L^3 (3,7-*diazanonane*-1,9-*diamine*) *or* L^4 (4,7-*diazadecane*-1,10-*diamine*)]. A partially neutralized solution of L with dilute HCl (1 g, pH *ca.* 7) was added to a hot freshly prepared solution of $[Ru(O_4C_2)_3]^{3-}$ and the pH of the resulting solution was adjusted to *ca.* 6.5 with either $Na_2[CO_3]$ or HCl as appropriate. The solution was refluxed for 2.5 h, treated with concentrated HCl (10 cm^3), and refluxed again for 0.5 h. The orange-brown solution was filtered whilst hot and the filtrate was concentrated down to *ca.* 25 cm^3. To the filtered cooled solution, a concentrated solution of Na[ClO$_4$] (10 cm^3) was added to precipitate out an orange solid. This was filtered off and recrystallized from dilute HCl (1 mol dm^{-3}) (yield 80%).

The purity of the new complexes was checked by comparing their i.r. and electronic absorption spectra with those of known complexes.[3]

trans-*Dibromo(tetramine)ruthenium*(III) *perchlorate, trans*-[RuLBr$_2$][ClO$_4$] (L = L^3 *or* L^4). These complexes were prepared by essentially the same method as that of *trans*-[RuLCl$_2$][ClO$_4$] described above except that HBr was used instead of HCl. The red crystals collected could be recrystallized from dilute HBr (yield 70%). The purity of *trans*-[RuL^{3}Br$_2$][ClO$_4$] was checked by comparing its i.r. and electronic absorption spectra with those of an authentic sample.[3] The salt *trans*-[RuL^{4}Br$_2$][ClO$_4$] is new and was analysed for purity (Found: C, 17.9; H, 4.2; Br, 29.7; N, 10.5. Calc. for $C_8H_{22}Br_2ClN_4O_4Ru$: C, 18.0; H, 4.2; Br, 29.9; N, 10.5%).

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] The ^{1}H n.m.r. spectrum of *cis*-[RuL^1(NCS)$_2$]·H$_2$O in S(CD$_3$)$_2$O was recorded with a JEOL FX90Q FT spectrometer.

RESULTS AND DISCUSSION

The methods reported here for the synthesis of *cis*-macrocyclic amine complexes of ruthenium are reproducible. There are several approaches for the synthesis of the starting substrate, [Ru(O$_4$C$_2$)$_3$]$^{3-}$. The classical methods involve the reaction between RuCl$_3$ {or K$_2$[RuCl$_5$(OH$_2$)]} and potassium oxalate in sealed tubes at 130 °C [7,8] or between RuCl$_3$ and oxalic acid at 100 °C.[10] However, it was found more convenient to generate [Ru(O$_4$C$_2$)$_3$]$^{3-}$ in solution by treating K$_2$[RuCl$_5$(OH$_2$)] with oxalic acid. Isolation of K$_3$[Ru(O$_4$C$_2$)$_3$] only served to reduce the yield since the complex is very soluble in water. Since [Ru(O$_4$C$_2$)$_3$]$^{3-}$ appeared to be rather unstable on standing in solution it should be freshly prepared before use.

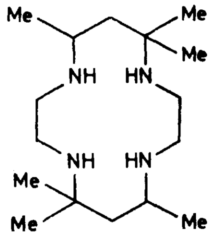
The reaction between [Ru(O$_4$C$_2$)$_3$]$^{3-}$ and L^1 is critically dependent on the pH of the solution. If the pH is greater than 9 or less than 4 the yield is very low. Some ill defined black solid usually appeared during the isolation of *cis*-[RuL^{1}Cl$_2$]Cl. Under suitably controlled conditions, the reaction between [Ru(O$_4$C$_2$)$_3$]$^{3-}$ and L^1 at pH *ca.* 6.5 very probably gives *cis*-[RuL^1(O$_4$C$_2$)]$^+$ as the intermediate. If Na[ClO$_4$] was added before the addition of concentrated HCl to the reaction solution, a yellow solid was precipitated, the i.r. spectrum of which clearly showed the presence of L^1, oxalate, and perchlorate. However, this method was not adopted for the synthesis of *cis*-[RuL^1(O$_4$C$_2$)][ClO$_4$] as some ill defined by-products were usually formed which were difficult to remove.

One of the major difficulties associated with the synthesis of *cis*-ruthenium(III) complexes of quadridentate amines is their relative ease of isomerization. Attempts have been made in vain to synthesize *cis*-[RuLCl$_2$]$^+$ (L = L^2, L^3, or L^4) by treating [Ru(O$_4$C$_2$)$_3$]$^{3-}$ with the corresponding quadridentate amine at various pH values ranging from 4 to 7. In every case, only the corresponding *trans* isomer was isolated in *ca.* 80% yield. Although the synthesis of these *trans*-dichloro-complexes, by the dropwise addition of a methanolic solution of the corresponding amine to a refluxing methanolic suspension of K$_2$[RuCl$_5$(OH$_2$)], has been reported previously,[3] the use of [Ru(O$_4$C$_2$)$_3$]$^{3-}$ as the starting material has certain advantages in that absolute methanol is not required. The method is particularly suitable for the direct synthesis of *trans*-[RuLBr$_2$]$^+$ (L = L^3 or L^4). The previous method [3] involved the reduction of the corresponding *trans*-[RuLCl$_2$]$^+$ with amalgamated zinc followed by reoxidation in the presence of an excess of bromide ion.

The reaction between [Ru(O$_4$C$_2$)$_3$]$^{3-}$ and L^1, surprisingly, gives *cis*-[RuL^{1}Cl$_2$]$^+$ in high yield and no isomerization has been detected in strong acidic solution. The stability of *cis*-[RuL^{1}Cl$_2$]$^+$ relative to the L^2 analogue with regard to isomerization may be due to the optimum ring size of L^1 which can comfortably hold the ruthenium(III) ion whether folded or unfolded. The ring-size effects on the geometric configuration of macrocyclic amine complexes have been demonstrated for the cobalt(III) system.[11]

From the reaction between [Ru(O$_4$C$_2$)$_3$]$^{3-}$ and L^2, only *cis*-[RuL^{2}Br$_2$]Br could be obtained in poor yield. Moreover, if the conditions, such as pH, were not carefully controlled, no *cis* isomer could be isolated, the corresponding *trans* isomer being formed in high yield.

Reactions between [Ru(O$_4$C$_2$)$_3$]$^{3-}$ and some methyl-substituted macrocyclic amines, such as L^5 and L^6 (C-*meso*- and C-*rac*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetra-azacyclotetradecane respectively), have been tried. So far, we have not been able to co-ordinate these bulky macrocyclic amines to the ruthenium(III) ion in a *cis* configuration.



L^5 (C-*meso*)

L^6 (C-*rac*)

For the synthesis of *cis*-[RuL^1(X)Y]$^+$ [(X)Y = Br$_2$, I$_2$, (Br)Cl, (NCS)$_2$, or oxalate], the method of direct ligand substitution was used. The ion *cis*-[RuL^{1}Cl$_2$]$^+$ can be easily converted into *cis*-[RuL^{1}Br$_2$]$^+$ in a strong acidic medium in nearly quantitative yield. This is to be contrasted with the reluctance of *trans*-[RuL^{1}Cl$_2$]$^+$ to be converted into *trans*-$[RuL^1Br_2]^+$ by direct ligand substitution.[3] For the synthesis of *cis*-$[RuL^1(Br)Cl]^+$ from *cis*-$[RuL^1Cl_2]^+$, care must be exercised not to overshoot the desired product and obtain *cis*-$[RuL^1Br_2]^+$ instead. The optimum reaction time was determined by following the electronic absorption spectrum of the reaction mixture. The appearance of a peak at *ca.* 500 nm is a good indication of the formation of *cis*-$[RuL^1Br_2]^+$ and once this peak has appeared the reaction should be quenched. In any case, the intensity of the peak at *ca.* 500 nm should never be allowed to exceed about one sixth of that at *ca.* 400 nm which corresponds to *cis*-$[RuL^1(Br)Cl]^+$. For the synthesis of *cis*-$[RuL^1I_2]^+$, overheating must be avoided and the reaction must be carried out in strong acidic conditions, otherwise ill defined by-products are formed. For the synthesis of *cis*-$[RuL^1(NCS)_2]^+$, *cis*-$[RuL^1Br_2]^+$ should be used as the starting material. Ill defined products, together with *cis*-$[RuL^1(NCS)_2][NCS]$, are usually obtained on treating *cis*-$[RuL^1Cl_2]^+$ with thiocyanate in an acidic medium. On the other hand, for the preparation of *cis*-$[RuL^1(NCS)_2]\cdot H_2O$, *cis*-$[RuL^1Cl_2]^+$ is a much better starting material than *cis*-$[RuL^1Br_2]^+$ and the reaction with thiocyanate should be carried out in a neutral medium. The reasons underlying the difference in behaviour of these two *cis*-dihalogeno-complexes towards thiocyanate in acidic and neutral media are not known. Reactions between *cis*-$[RuL^1X_2]^+$ (X = Cl or Br) and an excess of $Na[N_3]$ were attempted. Addition of hexafluorophosphate to the reaction mixture gave a yellowish brown solid. However, the solid was very unstable and its spectrum indicated that it was not a simple diazido-complex of ruthenium(III) and L^1.

TABLE 1

Infrared spectra [a] in the 3 000—3 200 and 750—950 cm^{-1} regions of some *cis*-ruthenium(III) complexes of L^1

Complex	NH stretch	CH$_2$ and/or NH vibration									
$[RuL^1Cl_2]Cl$	3 170s, 3 050s	930w		895w	868s	850s	840m (sh)		810m	800s	
$[RuL^1Br_2]Br\cdot 0.5H_2O$	3 145m, 3 060s	930w		890w	868s	850s	845w (sh)		810m	800s	
$[RuL^1(Br)Cl]Br$	3 150m, 3 060s	930w		892w	868s	850s	842w (sh)		810m	800s	
$[RuL^1I_2]I\cdot H_2O$	3 115m (sh), 3 080m	930w			865m	850m	845w (sh)		810w	800m	
$[RuL^1(NCS)_2][ClO_4]$	3 200s, 3 100w	932m		898w	864m	850m	845w (sh)	832w [b]	810m (sh)	802m	
$[RuL^1(O_4C_2)][ClO_4]$	3 230s, 3 100s	935w	905w	890w	870m	858m	840w		810m (sh)	800s	
$[RuL^1(NCS)_2]\cdot H_2O$	3 200m, 3 140m	930w		900w	862m	850m			810m (sh)	800s (sh)	780s [b]

[a] s = Strong, m = medium, w = weak, and sh = shoulder. [b] ν(C–S) stretch of *N*-bonded thiocyanate.

All the new complexes are highly coloured and appear to be indefinitely stable in the dry solid state. The light yellow *cis*-$[RuL^1Cl_2]Cl$ gradually turned greyish green on exposure to moisture. The purity of each complex was confirmed by the observation that the electronic absorption spectrum was unaffected by recrystallization or repeated preparation. In some cases, this was confirmed by adsorbing the complexes on a Dowex 50W-X8 (20—50 mesh) cation exchanger in the acid form. Only a single band developed which could be eluted. Magnetic moments confirm that all the ruthenium(III) complexes are low spin ($\mu_{\text{eff.}} \approx 2.1$ B.M. at 298 K) * and the ruthenium(II) complex, *cis*-$[RuL^1(NCS)_2]\cdot H_2O$, is diamagnetic. Conductivity measurements confirm that *cis*-$[RuL^1(O_4C_2)][ClO_4]$ and *trans*-$[RuL^4Br_2][ClO_4]$ are 1 : 1 electrolytes in aqueous solution (molar conductivities 105 and 110 Ω^{-1} cm^2 mol^{-1} respectively) and *cis*-$[RuL^1(NCS)_2]\cdot H_2O$ is a non-electrolyte in methanol. All the other *cis*-ruthenium(III) complexes, are, however, too unstable in solution to enable their conductivities to be determined.

The geometrical configuration of these complexes was assigned on the basis of i.r. spectroscopy. The spectra of the L^1 complexes in the regions of interest are collected in Table 1. In the 750—950 cm^{-1} region, a consistent variation between the *cis* and *trans* isomers of L^1 complexes has been observed and found to be quite independent of the nature of the central metal ion, other ligands, and counter ions.[2,3,12,13] Those complexes assigned a *trans* configuration showed two groups of bands separated by $\geqslant 70$ cm^{-1}. The group at lower frequency, which arises essentially from the methylene vibration,[12] consisted of one sharp band near 800 cm^{-1}, while the group at higher frequency, which is due predominantly to the secondary amine vibration,[12] consisted mainly of two bands near 900 cm^{-1}. For the less symmetrical *cis* isomers the methylene vibration invariably showed two bands in the 790—830 cm^{-1} region, while the amine vibration gave at least three bands at lower frequency (840—900 cm^{-1}) and hence closer to the methylene bands than those of the *trans* isomers. It is thus clear from Table 1 that all the L^1 complexes prepared here have a *cis* configuration. This is, in fact, the only geometrical configuration for *cis*-$[RuL^1(O_4C_2)][ClO_4]$. The assignment of a *cis* configuration is supported by the far-i.r. spectrum of *cis*-$[RuL^1Cl_2]Cl$. A comparison of this spectrum with that of *cis*-$[RuL^1Br_2]Br$ enabled the ν(Ru–Cl) stretch to be assigned at 320s,

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* Throughout this paper: 1 B.M. $\approx 9.27 \times 10^{-24}$ A m^2.

302s, and 290s cm^{-1}, which is to be contrasted with the single ν(Ru–Cl) stretch at 322s cm^{-1} for *trans*-[RuL^{1}Cl$_2$]-Cl.[3] The corresponding ν(Ru–Br) and ν(Ru–I) stretches for *cis*-[RuL^{1}Br$_2$]Br and *cis*-[RuL^{1}I$_2$]I respectively fall on or below our instrumental limit of 200 cm^{-1} and, therefore, they could not be determined. The splitting pattern of the ν(N–H) stretch at *ca.* 3 100 cm^{-1} is also consistent with a *cis* configuration of these complexes. A *cis* configuration was also indicated by the ^{1}H n.m.r. spectrum of the diamagnetic *cis*-[RuL^1(NCS)$_2$]·H$_2$O in S(CD$_3$)$_2$O. Here, there are two relatively broad signals of equal intensity centred at *ca.* 8.3 and 5.3 p.p.m., assignable to the two sets of amine protons of L^1 in a folded configuration. The corresponding signals for the well characterized *cis*-[CoL^1(OH$_2$)$_2$]$^{3+}$ in DCl occur at *ca.* 7.5 and 5.5 p.p.m.[14]

The ambidentate thiocyanate ligand in *cis*-[RuL^1-(NCS)$_2$][ClO$_4$] and *cis*-[RuL^1(NCS)$_2$]·H$_2$O has been shown to be *N*-bonded since the ν(C–S) vibrations at 832 and 780 cm^{-1} respectively are too high for the value expected for an *S*-bonding mode.[15] The ν(Ru–NCS) stretch for the former complex occurs at 300s and 390s (sh) cm^{-1} whereas that for the latter could not be determined here as it might lie near or below 200 cm^{-1}.

The electronic absorption spectral data for the *cis*-L^1 complexes are collected in Table 2. These are dominated by charge-transfer transitions. The lowest-energy bands are essentially ligand-to-metal in nature, as confirmed by the gradual red shift of $\lambda_{max.}$ from chloro- through bromo- to iodo-complexes.

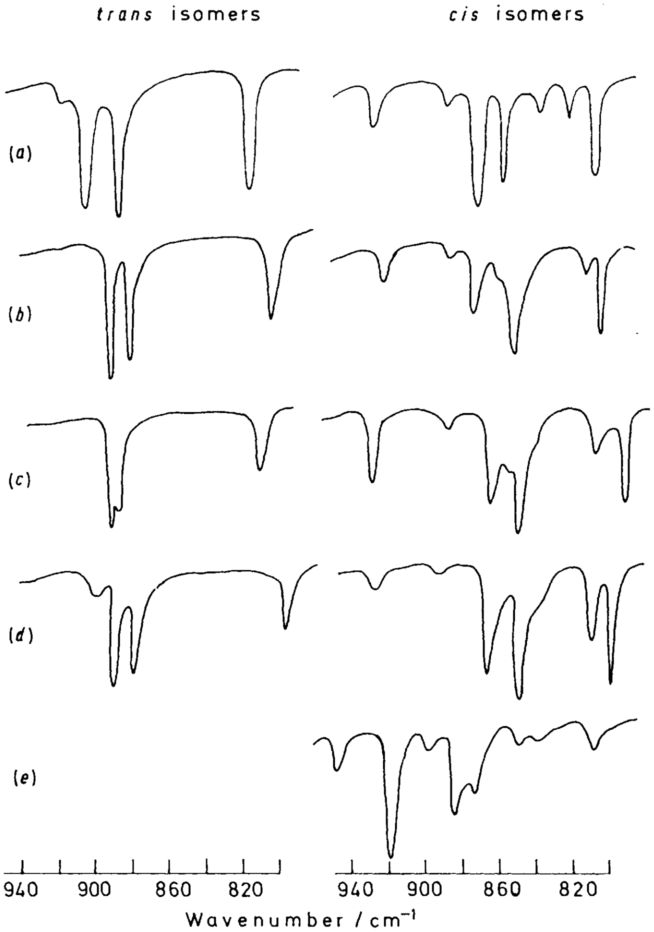
TABLE 2

Visible and u.v. absorption spectra of some *cis*-tetramine ruthenium complexes

Complex	Solvent	$\lambda_{max.}$ [a]/nm
[RuL^{1}Cl$_2$]Cl	HCl [b]	380br (1 070), 336br (1 480), 276br (950)
[RuL^{1}Cl$_2$]Cl [c]	HCl [d]	363 (280), 300 (sh) (530)
[Ru(en)$_2$Cl$_2$]Cl·H$_2$O [e]	HCl [b]	354 (1 750), 314 (1 420), 269 (900)
[Ru(pd)$_2$Cl$_2$]Cl [f]	HCl [g]	354 (1 640), 312 (1 480), 273 (880)
[RuL^{1}Br$_2$]Br·0.5H$_2$O	dmso [h,i]	505 (1 060), 401 (2 090), 322br (920)
[RuL^1(Br)Cl]Br	dmso [h,i]	*ca.* 447br (sh) (400), 400 (1 380), 345 (1 420)
[RuL^{1}I$_2$]I·H$_2$O	dmso [h,i]	*ca.* 570br (sh) (1 100), 520 (1 740), 350 (sh) (1 630)
[RuL^1(O$_4$C$_2$)][ClO$_4$]	H$_2$O	*ca.* 364br (sh) (830), 290 (2 030), 260br (1 920)
[RuL^1(NCS)$_2$][ClO$_4$]	dmso [h,i]	590br (3 640), 500br (3 670), *ca.* 370br (sh) (1 320), 331br (1 650)
[RuL^1(NCS)$_2$]·H$_2$O	dmso [h]	476 (1 630), 379 (2 940)
[RuL^{2}Br$_2$]Br	dmso [h,i]	500 (1 600), 410 (1 740), 381 (sh) (1 360), 322br (1 200)

[a] Molar absorption coefficients (ϵ/dm^3 mol^{-1} cm^{-1}) are given in parentheses; br = broad, sh = shoulder. [b] 1.0 mol dm^{-3}. [c] Ref. 6. [d] 0.1 mol dm^{-3}. [e] en = Ethane-1,2-diamine; ref. 19. [f] pd = Propane-1,3-diamine; ref. 19. [g] 0.05 mol dm^{-3}. [h] dmso = Dimethyl sulphoxide. [i] Acidified with toluene-*p*-sulphonic acid (0.1 mol dm^{-3}).

The assignment of a *cis* configuration to *cis*-[RuL^{2}Br$_2$]-Br was made mainly on the basis that its electronic absorption spectrum (Table 2) is very similar to that of *cis*-[RuL^{1}Br$_2$]Br but is distinctly different from that of *trans*-[RuL^{1}Br$_2$]Br.[3] The i.r. spectrum in the range 750—950 cm^{-1} is also very similar to that of all the *cis*-L^1 complexes, with a doublet near 800 cm^{-1} (802w and 815m) and four bands in the 840—900 cm^{-1} region (842w, 860m, 870m, and 880m cm^{-1}). As for the new complex *trans*-[RuL^{4}Br$_2$][ClO$_4$], its i.r. spectrum is virtually identical to that of *trans*-[RuL^{3}Cl$_2$][ClO$_4$],[3] hence the assignment of the *trans* configuration.



Infrared spectra (800—950 cm^{-1}) of some *cis*- and *trans*-[ML^{1}Cl$_2$]$^+$ complexes: (*a*) [CoL^{1}Cl$_2$]Cl; (*b*) [CrL^{1}Cl$_2$]Cl; (*c*) *cis*-[FeL^{1}Cl$_2$]Cl and *trans*-[FeL^{1}Cl$_2$][ClO$_4$]; (*d*) [RuL^{1}Cl$_2$]Cl, this work; (*e*) *cis*-[RuL^{1}Cl$_2$]Cl, ref. 6

Isied[6] very recently reported the isolation of *cis*-[RuL^{1}Cl$_2$]Cl as a by-product of the reaction between K$_2$[RuCl$_5$(OH$_2$)] and L^1 in methanol carried out according to the method of Chan *et al.*[2] We have not been able to repeat his method of isolating *cis*-[RuL^{1}Cl$_2$]Cl. In fact, our earlier method[2] for the synthesis of *trans*-[RuL^{1}Cl$_2$]Cl has recently been modified[3] and the experimental difficulties associated with the previous method[2] were due to metal-promoted ligand dehydrogenation and the formation of polymeric oxoruthenium species.[3] Despite the elaborate procedures employed, the report that the solid species obtained was *cis*-

$[RuL^1Cl_2]Cl$ was in question. The i.r. spectrum[6] of Isied's solid in the discriminating 800—950 cm^{-1} region is reproduced in the Figure, together with those of the well characterized *cis* and *trans* isomers of $[ML^1Cl_2]Y$ [M = cobalt(III),[14,16] chromium(III),[17,18] iron(III),[13] or ruthenium(III);[2,3] Y = Cl or ClO_4]. It is obvious that the i.r. spectrum of *cis*-$[RuL^1Cl_2]Cl$ reported here is very similar to those of the other three *cis* isomers of Co^{III}, Cr^{III}, and Fe^{III}, but that of Isied's solid is quite different. Furthermore, the electronic absorption spectrum of Isied's species also differs from the general pattern[19] of *cis*-$[RuLCl_2]Cl$ [L = L^1, bis(ethane-1,2-diamine), or bis-(propane-1,3-diamine)]. These u.v. spectra are also included in Table 2. It is obvious that all the well characterized *cis*-dichloro(tetramine) complexes show two ligand-to-metal charge-transfer bands above 300 nm with molar absorption coefficients (ε) greater than 1 000 and a band near 270 nm with ε *ca.* 900 $dm^3 mol^{-1} cm^{-1}$. The absorption spectrum of Isied's species looks very different. The ε values (200—500 $dm^3 mol^{-1} cm^{-1}$) for the bands above 300 nm are too low to be consistent with what would have been expected for ligand-to-metal charge-transfer transitions.

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