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# Supramolecular structures and properties models of macrocyclic polymer complexes

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**Two novel supramolecular complexes of types [Ru(L)($H_2L$)Cl·$OH_2$] and [Ru($HL_n$)$Cl_3$] (where $H_2L$ is a potential tetradentate ligand derived from hydrazine hydrate and diethyl malonate, and $HL_n$ is a potential bidentate ligand derived from coupling of allyl azo-$\beta$-diketone) have been synthesized and characterized by elemental analysis, conductance and magnetic measurements, followed by $^1H$ NMR, to determine the effect of substituents on the intramolecular hydrogen bond. The electronic properties and models of the bonding of ligands and complexes were investigated by UV–Vis and IR spectroscopies. The first type of complex contains terminal hydrazinic nitrogen atoms with an unshared electron pair and may take part in nucleophilic condensations. Therefore, the reactions of allyl-$\beta$-diketone complexes with malonic dihydrazide have also been studied, as these cause ring closure and formation of supramolecular macrocyclic ligand complexes. The wavelengths of the principal electronic absorption peaks have been accounted for quantitatively in terms of crystal field theory, and various parameters have been evaluated. On the basis of the electronic spectra, an octahedral geometry has been established for the polymer complexes C. The macrocyclic polymer complexes D are pentacoordinate, and a trigonal-bipyramidal environment ($D_{3h}$) is suggested for the ruthenium(III) ion. The effect of the Hammett constant on the ligand field parameters is also discussed. Copyright © 2004 John Wiley & Sons, Ltd.**

**KEYWORDS:** supramolecular structures; ruthenium(III); macrocyclic polymer complexes; Hammett constant; ligand field parameters

## INTRODUCTION

Within the area of coordination chemistry, complexes with chelating ligands generally have increased stability relative to those of monodentate ligands, and even greater stability when the donor atoms are incorporated into a cyclic ligand that surrounds the metal ion (i.e. a macrocyclic ligand). Some macrocyclic ligands can be made only in poor yields. To overcome this, use is made of the 'template effect', i.e. whereby the metal coordinates and may arrange the ligand precursor fragments in its coordination sphere, thereby assisting in the linking process that produces the macrocyclic polymer complexes.

The supramolecular assembly approach, based on coordination compounds, is primarily directed by the metal–ligand affinities, stereochemistry and substitution properties of the complexes involved. Another interesting property of supramolecular assembly polynuclear homopolymers is their ability to form homogeneous and adherent molecular films. From the many interesting supramolecular systems that have been reported in the literature,[1] we have focused on homopolymer uranium and ruthenium complexes, which have been systematically investigated in our laboratory.[2,3] Owing to the diversity of $HL_n$ azodyes and their wide application in many fields (medicine, analytical chemistry, etc.), efforts have been made to carry out detailed studies to elucidate the structural and electronic properties of these ligands and their complexing affinities toward different transition metals.[2–5] Since we could not find information on ruthenium(III) polymer and macrocyclic polymer complexes with $HL_n$ in the literature, we have prepared and characterized them using various physico-chemical techniques.

The number and relative positions of the donor atoms and the cavity size in macrocyclic compounds confer with special

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reactivities on these molecules. From specific dicarbonyl and diamine precursors, the structure of the condensation product is conditioned by controlling the reaction conditions.[6]

The role played by azo polymer and/or macrocyclic complexes in various systems means that elucidating the nature of their metal binding and stereochemistry is of great interest. These azo polymer and/or macrocyclic compounds have also elicited much attention because of their use as models of biological systems.[7] Consequently, we have investigated the coordinating behaviour and chemical equilibria of some of these azo and azo polymer compounds.[3–5]

In this paper, the results of $^1H$ NMR, IR, and electronic spectroscopic studies and magnetic measurements are presented and discussed. The effect of the Hammett constant on the ligand field parameters was also investigated.

## EXPERIMENTAL

The experimental techniques have been described previously.[2–5]

### Synthesis of ligands

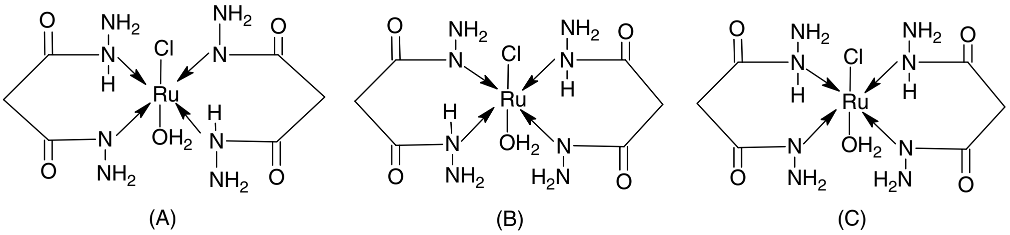
The standard chemicals, allyl-$\beta$-diketone, malonyl dihydrazide, aniline and 4-alkyl-anilines (alkyl: $OCH_3$, $CH_3$, Cl, $NO_2$; Aldrich Chemical Co.) were used without any further purification, and 2,2′-azobisisobutyronitrile (AIBN; Eastman Kodak) was purified by recrystallization from EtOH.[8]

### Preparation of ruthenium dihydrazide complex

Alcoholic solution mixtures of ruthenium chloride (0.02 mol) and the appropriate malonyl dihydrazide (0.02 mol) were refluxed together for 3–4 h. The product obtained (Scheme 1) was filtered off and washed with hot (1 : 1) ethanol : water to remove any excess of the metal salt and the ligand. Yield ~65%. Anal. Found: C, 17.2; H, 3.9; N, 27.1. Calc. for $(C_3H_8N_4O_2)_2RuCl\cdot H_2O$ (MW = 416.6): C, 17.3; H, 3.8; N, 26.9%. The ligand and complex were characterized by IR spectroscopy (Table 1).

### Preparation of 3-[(4-derivatives phenyl) diazenyl]-1-(vinyloxy)pentane-3,4-dione ($HL_n$)

In a typical preparation, 25 ml of distilled water containing hydrochloric acid (12 M, 2.68 ml, 32.19 mmol) was added to aniline (0.979 ml, 10.73 mmol) or a 4-alkyl aniline. To the resulting mixture, stirred and cooled to 0 °C, a solution of sodium nitrite (740 mg, 10.73 mmol, in 20 ml of water) was added dropwise. The diazonium chloride formed was consecutively coupled with an alkaline solution of allylacetoacetate (0.142 mg, 10.73 mmol) in 20 ml of pyridine. The precipitate (yield 60%), which formed immediately, was filtered, washed several times with water and purified by recrystallization from hot ethanol (Scheme 2). The analytical

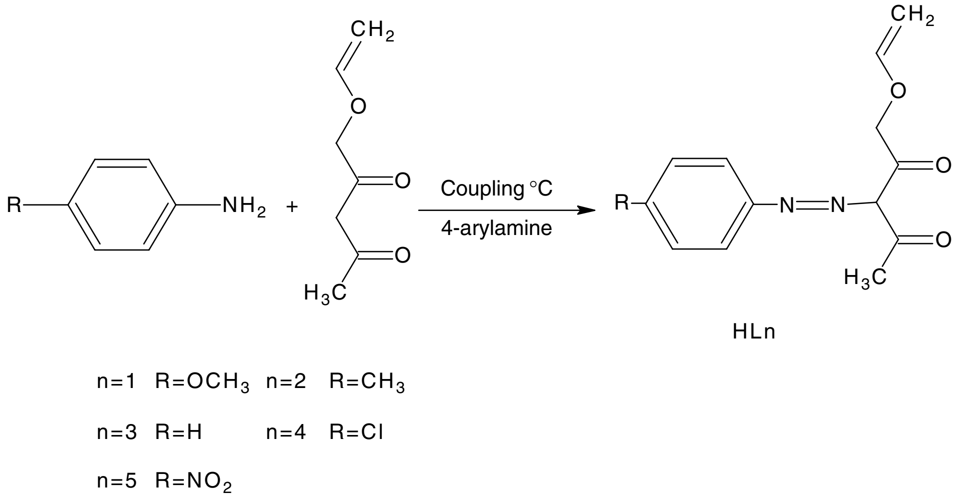


**Scheme 1.** Coordination of $H_2L$ with $RuCl_3\cdot 3H_2O$.

**Table 1.** Important IR spectra bands ($cm^{-1}$) of the ligand and the complexes together with tentative assignments (for molecular structures see Schemes 1 and 4)

| | | | Amide-I | Amide-II | Amide-III | |
|---|---|---|---|---|---|---|
| Composition[a] | $\nu$ (OH) | $\nu_{asm}$ (NH) | $\nu$ (CO) | $\nu$(CN) + $\delta$(NH) | $\nu$ (NH) | $\nu$ (C=N) |
| $H_2L$[b] | | 3140 | 1685 | 1520 | 1260 | — |
| $[Ru(L)(H_2L)Cl(OH_2)]$ | 3445 | 3152 | 1678 | 1465 | 1240 | — |
| **A** | | | | | | |
| **6** | — | 3148 | 1693 | 1470 | 1453 | 1617 |
| **7** | — | 3143 | 1682 | 1475 | 1252 | 1612 |
| **8** | — | 3141 | 1680 | 1473 | 1250 | 1610 |
| **9** | — | 3139 | 1677 | 1474 | 1251 | 1605 |
| **10** | — | 3140 | 1681 | 1478 | 1253 | 1607 |

[a] Complex details are listed in Table 2.
[b] $H_2L{=}CH_2[C(O)NHNH_2]_2$.



**Scheme 2.** General formula and proton numbering scheme of the 3-[(4-derivatives phenyl]-1-(vinyloxy)pentane-2,4-dione ($HL_n$).

data confirmed the expected compositions (Table 2). The ligands were also characterized by IR and $^1$H NMR spectroscopy (Tables 3 and 4).

## Synthesis of the polymer complexes

A 50 ml portion of a 0.5 M solution of the salt in dimethylformamide (DMF) was mixed with 50 ml of the monomer (0.1 M) in the same solvent and 0.1 w/v AIBN as initiator. The mixture was stirred under reflux for ~8 h and the resulting polymer complexes were precipitated by addition of dilute hydrochloric acid (20 mmol/25 ml distilled water) until around pH 5.5 was reached, to ensure the removal of excess metal salt (Scheme 3). The precipitate was filtered off, washed with water and dried in a vacuum oven at 40 °C for several days.

## Synthesis of the macrocyclic polymer complexes

To a suspension of the polymer complexes $[RuHL_nCl_3]$ (0.02 mol) in 100 ml EtOH : DMF (2 : 1, v/v) and glacial AcOH (2 mol), a diamine (0.02 mol) in 20 ml of the same solvent was added. The mixture was refluxed with stirring for ~9 h. Upon cooling, the solid obtained (55% yield) was filtered off, washed several times with hot $H_2O$ : EtOH (1 : 1, v/v) and dried in a vacuum oven at 40 °C for several days (Scheme 4).

## Measurements

Carbon, hydrogen and nitrogen microanalyses were carried out at King Khalid University Analytical Center, Saudi Arabia, using a Perkin Elmer 2400 Series II Analyzer. The metal content in the polymer complexes was estimated by standard methods.[2–5] The $^1$H NMR spectrum was obtained using a JEOL FX900 Fourier transform spectrometer with deuterated dimethylsulfoxide (DMSO-$d_6$) as the solvent and tetramethylsilane (TMS) as an internal reference. IR spectra were recorded using a Perkin–Elmer 1340 spectrophotometer. UV–Vis spectra of the polymer were recorded in Nujol solution using a Unicam SP 8800 spectrophotometer. The magnetic moments of the solid complexes prepared were determined at room temperature using the Gouy method. Mercury(II) (tetrathiocyanato)cobalt(II), $[Hg\{Co(SCN)_4\}]$, was used for the calibration of the Gouy tubes. Magnetic moments were calculated using the equation $\mu_{\mathrm{eff}} = 2.84(T_{\chi_M}^{\mathrm{coor}})^{1/2}$. The halogen content was determined by combustion of the solid complex (30 mg) in an oxygen flask in the presence of a $KOH–H_2O_2$ mixture. The halide content was then determined by titration with a standard $Hg(NO_3)_2$ solution using diphenyl carbazone as an indicator.

# RESULTS AND DISCUSSION

The ligands and metal polymer and/or macrocyclic polymer complexes under study were labeled as shown in Table 2 and Schemes 3 and 4. The subject of polymer complexes has grown extensively, stimulated by interest in their application to physico-chemical studies, catalysis and bioinorganic chemistry.[8,9] The stoichiometries (1 : 2, metal : ligand) of complex **A** and (1 : 1, metal : ligand) of polymer complexes **1–10** were established principally by elemental analysis. The microcrystalline complexes are partially soluble in DMF and DMSO. The molar conductivities, obtained in DMF demonstrate that all the reported complexes are non-electrolytes, with $\Lambda_M$ lying in the 12.4–20.7 $\Omega^{-1}$ cm$^2$ mol$^{-1}$ range. The Experimental section lists 10 new polymeric complexes, and their elemental analyses agree with the assigned formulae. The formation of the representative polymer complexes can be summarized thus:

$$RuCl_3{\cdot}3H_2O + H_2L \longrightarrow [Ru(L)(H_2L)Cl{\cdot}OH_2] \qquad (\mathbf{A})$$

$$RuCl_3{\cdot}3H_2O + HL_n \longrightarrow [Ru(HL_n)Cl_3] \qquad (\mathbf{1–5})$$

$$[Ru(HL_n)Cl_3] + H_2L \longrightarrow [Ru(HL'_n)Cl_3] \qquad (\mathbf{6–10})$$

**Table 2.** Analytical data for ruthenium(III) polymer complexes[a] of 3-[(4-derivatives phenyl)diazenyl]-1-(vinyloxy)pentane-3,4-dione ($HL_n$); for molecular structures see Schemes 1–4[b]

| Composition[c] | Code | Structure | Preparation method | Experimental (Calc.) (%) C | H | N | Cl |
|---|---|---|---|---|---|---|---|
| $HL_1$ | **1** | **C** | Scheme 2 | 61.0 | 5.7 | 10.4 | — |
| | | | | (60.9) | (5.8) | (10.2) | — |
| $[Ru(HL_1)Cl_3]$ | | | Scheme 3 | 34.8 | 3.2 | 6.0 | 21.8 |
| | | | | (34.7) | (3.3) | (5.8) | (22.0) |
| $HL_2$ | **2** | **C** | Scheme 2 | 64.5 | 6.1 | 11.0 | — |
| | | | | (64.6) | (6.2) | (10.8) | — |
| $[Ru(HL_2)Cl_3]$ | | | Scheme 3 | 36.0 | 3.5 | 5.8 | 23.0 |
| | | | | (35.9) | (3.4) | (6.0) | (22.8) |
| $HL_3$ | **3** | **C** | Scheme 2 | 63.5 | 5.6 | 11.6 | — |
| | | | | (63.4) | (5.7) | (11.4) | — |
| $[Ru(HL_3)Cl_3]$ | | | Scheme 3 | 34.3 | 3.0 | 6.0 | 23.3 |
| | | | | (34.4) | (3.1) | (6.2) | (23.5) |
| $HL_4$ | **4** | **C** | Scheme 2 | 47.9 | 3.9 | 8.8 | — |
| | | | | (48.0) | (4.0) | (8.6) | — |
| $[Ru(HL_4)Cl_3]$ | | | Scheme 3 | 31.8 | 2.5 | 5.5 | 29.4 |
| | | | | (32.0) | (2.7) | (5.7) | (29.1) |
| $HL_5$ | **5** | **C** | Scheme 2 | 53.5 | 4.6 | 14.6 | — |
| | | | | (53.6) | (4.5) | (14.4) | — |
| $[Ru(HL_5)Cl_3]$ | | | Scheme 3 | 31.2 | 2.5 | 8.1 | 21.1 |
| | | | | (31.3) | (2.6) | (8.4) | (21.4) |
| $[Ru(HL'_1)Cl_3]$ | **6** | **D** | Scheme 4 | 35.1 | 3.6 | 14.7 | 18.1 |
| | | | | (35.2) | (3.5) | (14.5) | (18.4) |
| $[Ru(HL'_2)Cl_3]$ | **7** | **D** | Scheme 4 | 36.1 | 3.5 | 15.2 | 19.3 |
| | | | | (36.2) | (3.6) | (14.9) | (18.9) |
| $[Ru(HL'_3)Cl_3]$ | **8** | **D** | Scheme 4 | 35.0 | 3.2 | 15.5 | 19.1 |
| | | | | (34.9) | (3.3) | (15.3) | (19.4) |
| $[Ru(HL'_4)Cl_3]$ | **9** | **D** | Scheme 4 | 33.0 | 3.0 | 14.1 | 18.5 |
| | | | | (32.9) | (2.9) | (14.0) | (18.2) |
| $[Ru(HL'_5)Cl_3]$ | **10** | **D** | Scheme 4 | 31.5 | 2.7 | 13.7 | 17.1 |
| | | | | (31.5) | (2.8) | (13.8) | (17.4) |

[a] Microanalytical data and metal estimations are in good agreement with the stoichiometry of the proposed complexes.

[b] The good agreement between calculated and experimental data supports the assignments suggested.

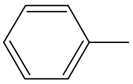
[c] L is the anion of $H_2L$; $HL_n$ and $HL'_n$ are the azomonomers as given in Schemes 2 and 4.

**Table 3.** Selected IR spectral data of the free ligand and ruthenium polymer complexes (for molecular structures see Scheme 3)

| Compound[a] | Frequency ($cm^{-1}$) $\nu$ C=N | $\nu$ NH | $\nu$ C–O–C | $\nu$ C=O | $\nu$ N=N | $\nu$ C=C |
|---|---|---|---|---|---|---|
| Ligand | — | — | 1080 | 1690–1640 | 1485–1445 | 1660–1630 |
| **1** | 1628 | 3330 | 1083 | 1685 | — | — |
| **2** | 1622 | 3290 | 1083 | 1670 | — | — |
| **3** | 1618 | 3270 | 1083 | 1665 | — | — |
| **4** | 1610 | 3220 | 1080 | 1650 | — | — |
| **5** | 1612 | 3240 | 1083 | 1642 | — | — |

[a] See Table 2.

**Table 4.** $^1$H chemical shift of $HL_3$ (ppm TMS)[a]

| Functional groups | $^1$H NMR (ppm) |
|---|---|
| $CH_2{=}CH—$ | 6.0–5.4 |
| $CH_2—$ | 4.8 |
| $CH_3—$ | 1.85 |
| CH | 3.61 |
|  | 7.1–7.45 |

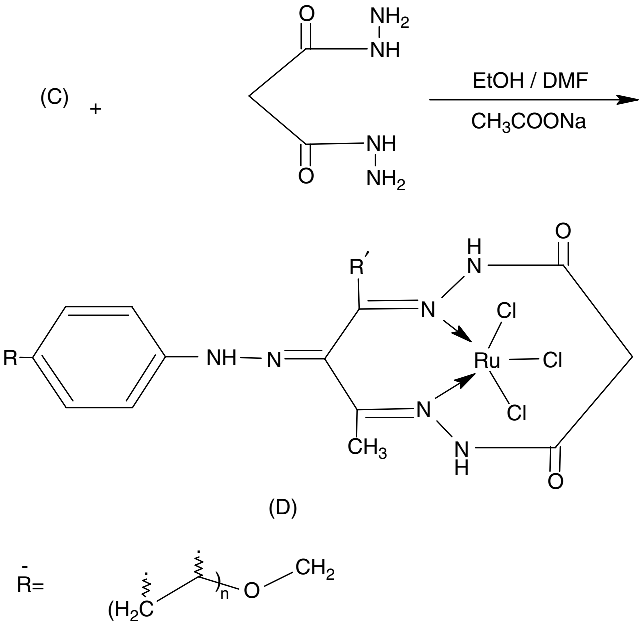
[a] The good agreement between the experimental data supports the assignments suggested in the present work.

## Magnetic measurements

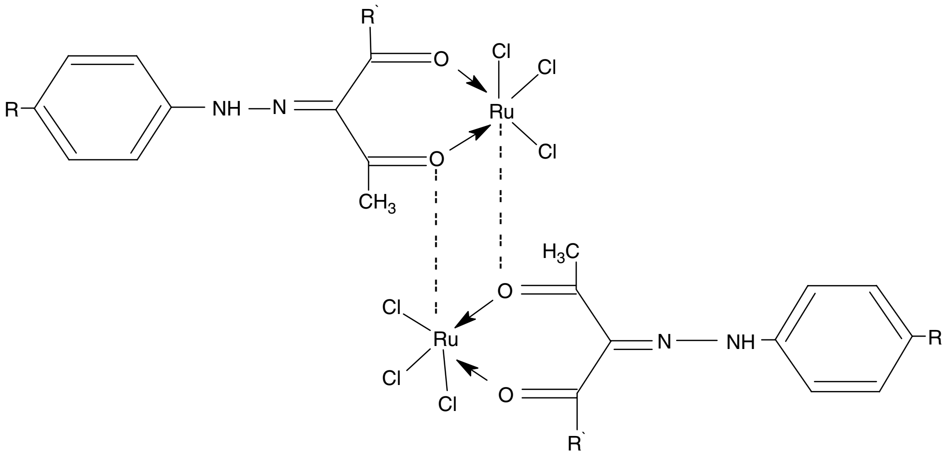
The magnetic moments of the ruthenium(III) azodye polymer complexes under study were measured at room temperature using the Gouy method. The observed magnetic moment $\mu_{\text{eff}}$ values are listed in (Table 5). They correspond to a spin quantum number $s = \frac{1}{2}$, as expected for the low-spin configuration $t_{2g}^5$ ruthenium(III) with one unpaired electron in an octahedral environment within the complexes. For complex **A**, the observed magnetic moment is slightly higher than the spin-only value for one unpaired electron (1.73 BM). This can be explained by the slight spin–orbit coupling to be expected in such cases. For polymer complexes **1**–**5**, the measured effective magnetic moments $\mu_{\text{eff}}$ are lower than the spin-only value. However, for complexes **6**–**10**, the room-temperature magnetic moments lie in the range 1.78–1.72 BM, i.e. lower than the predicted (2.1 BM) value. This might be indicative of an exchange interaction between two neighbouring ruthenium ions of $d^5$ configuration in the polymeric structure, and also due to low symmetry.

## Electronic absorption spectra

Octahedral low-spin $d^5$ polymer complexes have the $^2T_{2g}$ ground state corresponding to the electronic state $t_{2g}^5$ and the first excited doublet levels will be $^2A_{2g}$ and $^2T_{1g}$.[10] The intensity band in the electronic spectra of the polymer complexes is assignable to the allowed charge-transfer transition (L → M) from the $\pi$ level of donor atoms to the incomplete metal $t_{2g}(\pi^*)$ level.[11] In the present complexes, three observed bands typical of octahedral ruthenium(III) polymer complexes originated from the ground term $^2T_{2g}$. These can be assigned[12] to $^2T_{2g} \rightarrow {}^2A_{2g}$ (15 000–16 400 cm$^{-1}$) ($\sigma_1$), $^2T_{2g} \rightarrow {}^2T_{1g}$ (16 100–17 600 cm$^{-1}$) ($\sigma_2$) and $^2T_{2g} \rightarrow {}^2E_g$ (20 000–22 300 cm$^{-1}$) ($\sigma_3$) transition in increasing order of energy, in addition to a shoulder at 30 100–37 777 cm$^{-1}$



**Scheme 4.** Molecular structure proposed for ruthenium(III) macrocyclic polymer complexes.



(c)

**Scheme 3.** Molecular structure proposed for ruthenium(III) polymer complex.

**Table 5.** Electronic spectral data and ligand field parameters ($cm^{-1}$) for ruthenium(III) polymer complexes

| Complex[a] | Bands (obs.) | Assignment | | $\mu_{eff(BM)}$ | $\nu_2/\nu_1$ | 10Dq | $B$ | $\beta$ | $C$ | $F_2$ | $F_4$ | $Z^*$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 14 600 | $\pi$ | $t_2g$ | | | | | | | | | |
| **A** | 16 685 | $\pi$ | eg | 1.98 | 1.14 | 19 600 | 384 | 0.697 | 1501.5 | 603.4 | 43.9 | 0.62 |
| | 23 100 | $\sigma$ | $t_2g$ | | | | | | | | | |
| | 16 260 | $\pi$ | $t_2g$ | | | | | | | | | |
| **1** | 19 760 | $\pi$ | eg | 1.65 | 1.215 | 21 260 | 416.8 | 0.705 | 1667.2 | 654.8 | 47.6 | 0.77 |
| | 24 610 | $\sigma$ | $t_2g$ | | | | | | | | | |
| | 16 200 | $\pi$ | $t_2g$ | | | | | | | | | |
| **2** | 19 780 | $\pi$ | eg | 1.62 | 1.22 | 21 200 | 415.7 | 0.695 | 1662.5 | 653.2 | 47.5 | 0.76 |
| | 24 490 | $\sigma$ | $t_2g$ | | | | | | | | | |
| | 16 125 | $\pi$ | $t_2g$ | | | | | | | | | |
| **3** | 19 600 | $\pi$ | eg | 1.59 | 1.22 | 21 125 | 414.2 | 0.704 | 1656.9 | 650.9 | 47.3 | 0.75 |
| | 24 400 | $\sigma$ | $t_2g$ | | | | | | | | | |
| | 16 020 | $\pi$ | $t_2g$ | | | | | | | | | |
| **4** | 20 000 | $\pi$ | eg | 1.50 | 1.25 | 21 020 | 412.2 | 0.689 | 1648.5 | 647.7 | 47.1 | 0.74 |
| | 23 800 | $\sigma$ | $t_2g$ | | | | | | | | | |
| | 15 150 | $\pi$ | $t_2g$ | | | | | | | | | |
| **5** | 17 580 | $\pi$ | eg | 1.55 | 1.16 | 20 150 | 395 | 0.614 | 1578.5 | 620.7 | 45.1 | 0.67 |
| | 24 230 | $\sigma$ | $t_2g$ | | | | | | | | | |
| | 12 300–13 300 | $^2A_1''$ | $^2E_1''$ | | | | | | | | | |
| **6–10** | 16 200–16 600 | $^2A_1''$ | $^2E'$ | 1.72–1.78 | | | | | | | | |
| | 22 000–22 300 | $^2A''_{(I)}$ | $^2A''_{2(II)}$ | | | | | | | | | |
| | 25 900–26 000 | | | | | | | | | | | |

[a] See Table 2.

(Table 5). The electronic spectra of these complexes are further rationalized in terms of ligand field parameters (10Dq) and interelectronic repulsion parameters ($B$ and $C$) using the following equations:[12]

$$^2T_{2g}(t^5) = 0$$

$$^4T_{1g}(t^4e) = 10Dq - 5B - 4C$$

$$^4T_{2g}(t^4e) = 10Dq + 3B - 4C$$

$$^2A_{2g}, {}^2T_{1g}(t^4e) = 10Dq - 2BC$$

The values of these parameters, given in (Table 5), are comparable to those reported for other ruthenium(III) derivatives involving oxygen donor molecules.[13] The spectral data were also utilized to compute the important ligand field parameters. The lower values of the Racah interelectronic repulsion parameter $B$ in comparison with the free-ion value indicate that a strong interaction occurs between the ligands and the central metal ion. In other words, the greater the reduction in $B$ the greater the covalency in the metal–ligand bond and the smaller the effective charge experienced by the d-electrons.[12] The overall effect of the covalent bonding will be an increase in the observed value of 10Dq. Such an increase in 10Dq values is generally associated with considerable electron delocalization.[14] Decreasing $\beta$ values are also associated with a reduction in the effective positive charge of the metal ion and with an increasing tendency to reduction to the next lower oxidation state. For second-row transition metals, the variation of the Racah interelectronic repulsion parameter with the cationic charge $Z^*$ and the number $q$ of electrons in the partially filled d-shell is expressed by the relation[15]

$$B(cm^{-1}) = 472 + 28q + 50(Z^* + 1) - 500/(Z^* - 1)$$

The effective ionic charges of the ruthenium(III) polymer complexes are in the range 0.62–0.77, which is considerably below the formal +3 oxidation state of the metal ion. It is apparent that the nephelauxetic ratio $\beta$ depends generally upon the electronegativity of the donor atoms and the ligand structure.

The electronic spectra of macrocyclic polymer complex derivatives of the type $[Ru(HL_n')Cl_3]_n$ (**6**–**10**) are different, with four bands at 12 300–13 300, 16 200–16 600, 22 000–22 300, and 25 900–26 000 $cm^{-1}$ (Table 5). These agree well with the one-electron orbital schemes for trigonal bipyramidal $d^5$ complexes. The first low-energy band at 12 300–13 300 $cm^{-1}$ is assigned to a one-electron transition from (e″) ($xz$, $yz$) to $a_1'(z^2)$ i.e. $^2A_1'' \rightarrow {}^2E_1''$. The next lower energy band may be due to allowed transitions $a_1'(z^2) \rightarrow e_1'$ $(x^2 - y^2, xy)$, i.e. $^2A_1' \rightarrow {}^2E_1'$. The remaining two bands are assigned to the allowed excited state $^2A_2''(I)$ and $^2A_2''(II)$, arising from the configuration $(e'')^3(a_1')(e')^1$.

As can be seen from Table 5, the Racah parameter $B$ values decreased from 1 to 5. This can be attributed to the fact that the effective charge experienced by the d electrons is decreased due to the electron-withdrawing para-substituted $HL_4$ and $HL_5$; whereas it is increased by the electron-donating character of $HL_1$ and $HL_2$. This is in accordance with that expected from the Hammett constant $\sigma^R$, which correlates with the Racah parameter; it is clear from Fig. 1a–d that all these parameters decrease with increasing $\sigma^R$.

The above results show clearly the effect of substitution in the para-position of the benzene ring on the stereochemistry of ruthenium(III) polymer complexes. It is important to note that the existence of a methyl and/or methoxy group enhances the electron density on the coordination sites and simultaneously increases the values of the Racah parameters (Table 5).

## IR spectra and nature of coordination

### *Reaction of ruthenium(III) with diamine ($H_2L$)*

The spectrum of present ligand exhibits bands at ~1685 cm$^{-1}$ [amide-I, $\nu$(CO)], 1530 (amide-II, $\nu(CN) + \delta(NH)$) and 1270 cm$^{-1}$ (amide-III, $\delta$(NH)). The trend of changes in various amide group vibrations in the complexes is consistent with the coordination of amide-nitrogen to metal atom[16] (Table 1). Since complex **A** is a nonelectrolyte and has 1 : 2 (metal : ligand) stoichiometry, it is apparent that the $H_2L$ ligand is coordinated to the ruthenium through deprotonated and through protonated amide-nitrogen atoms. The ligand bands observed at *ca* 3200 cm$^{-1}$ and 1685 cm$^{-1}$ are due to $\nu$(NH) and $\delta(NH_2)$ vibrations respectively. These bands remain unchanged in the complex, thus indicating noncoordination of the terminal hydrazinic nitrogen atoms to the metal. The new bands at *ca* 3400 cm$^{-1}$, 1630 cm$^{-1}$, 890 cm$^{-1}$ and 870 cm$^{-1}$ are assignable to $\nu$(OH), Qr($H_2O$), $\delta(H_2O)$ and Qw($H_2O$) vibrations[17] respectively, indicating the presence of coordinated water.

Different structures are possible for this complex depending upon whether or not the two amide groups in the same ligand are deprotonated, i.e. as opposed to one each from two different ligand molecules. As mentioned previously, the complex can be depicted by the structures **A**, **B** and **C** in Scheme 1.

### *Reaction of ruthenium(III) with azo-homopolymer ($HL_n$)*

By tracing the IR spectra of azo polymer compounds, no $\nu(NH_2)$ stretching vibrations are apparent. This supports the formation of azodye ligands. The mode of bonding of the $HL_n$ to the metal ion was elucidated by investigating the IR spectra of the complexes on the basis comparative analysis of the results with respect to literature data of related systems. The positions of the most relevant and characteristic bands are due to the two carbonyl atoms. The spectra exhibit a medium to strong band in the region 1400–1500 cm$^{-1}$, which is tentatively assigned to $\nu$(N=N) stretching vibrations.[3,5]

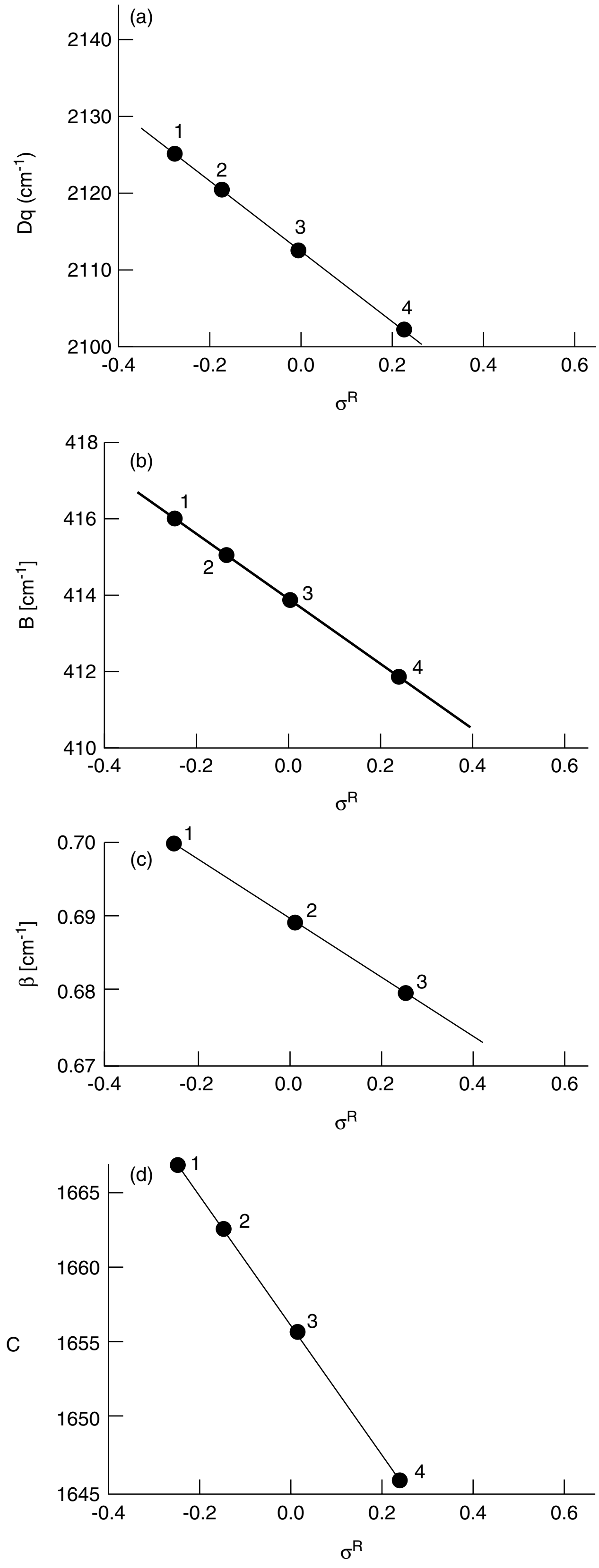


**Figure 1.** The variation of para-substituted Hammett's constant with (a) Dq, (b) $B$, (c) $\beta$ and (d) $C$.

The C═C stretching vibrations of the phenyl ring are located at 1500–1600 $cm^{-1}$, which are due to the symmetric and assymmetric vibrations.

The most important bands in the IR spectra of the polymer complexes are assigned to vibrations of the ligands in accordance with published data.[18,19] The main differences are those relating to CO vibrations, suggesting that coordination has been effected.

3-[(4-Derivatives phenyl)diazenyl]-1-(vinyloxy)pentane-2, 4-dione ($HL_n$) is a ligand whose reactivity toward metal ions varies as a function of the 4-substituents. The products formed are neutral, with two coplanar *O,O* metal-chelate rings in an *O,O* geometry. Consequently, in the ruthenium(III) case, the ruthenium atom should be six-coordinate octahedral with the oxygen atom in the apical position of the ligand. The high polymer chemistry of $HL_n$ has become increasingly important, with considerable emphasis being placed on the chemistry and uses of organometallic derivatives.[3,18,19] This difference in reactivity and protonation of the CH group (Scheme 2), which result from the effect of substituents in the para position of the phenyl azo group of heterocycles, has been the subject of detailed investigations.

In general, the presence of an electron-attracting group minimizes the charge transfer from the phenyl ring, and this leads to increasing of the CO band modes. The strong presence of three bands located at 2995, 2960 and 2855 $cm^{-1}$ indicates the existence of a methoxy group ($HL_1$). The $\beta$(C–H) and $\nu$(C–H) modes of vibrations are identified by the presence of strong bands in the ranges 1180–1110, 1030–930 $cm^{-1}$ and 840–780 $cm^{-1}$ respectively. The C–C vibrations are also identified by the presence of several bands at frequencies just after 750 $cm^{-1}$. Generally, the electron donor methoxy group enhances the charge transfer from the phenyl ring to the heterocyclic moiety. This leads to an increase in polarizability of the carbonyl group. Meanwhile, the methyl group attached to aromatic rings has been studied in details.[20] The three bands located at ~1495, 1455 and ~1425 $cm^{-1}$ are due to methyl deformation for C–H bending absorption expected to be present in the ligand ($HL_2$). From the spectra and the frequency data in (Table 3), it can be concluded that the mode of bonding of ruthenium(III) to the $HL_n$ ligand depends to some extent on the molecular structure of the ligand itself.

(1) The $\nu$(C═O) displays a band shift to lower wavenumbers in the spectra of the polymer complexes and the intensities of the bands are also reduced. In addition to giving an indication about the contribution of the carbonyl oxygen in coordination to the ruthenium atom, the lowering of the CO frequency can be considered as support for the participation of the $HL_n$ in coordination to ruthenium(III) as a neutral bidentate ligand.
(2) The spectra also display bands due to Ru–Cl, which are in agreement with the assumption that the ruthenium is coordinated to the three chloride ions.
(3) It is interesting to note that polymer complexes **1**–**5** do not exhibit bands characteristic of coordinated water molecules.
(4) Therefore, in these polymer complexes **1**–**5**, interaction of ruthenium(III) ions with the free electron pairs of the oxygen atoms of a neighbouring complex molecule confers coordination saturation in the octahedral configuration (Scheme 3); this interaction mode has been identified in analogous ruthenium complexes.[21]
(5) The bonding of the ruthenium(III) to the ligand through oxygen and chlorine is confirmed by the appearance of the two new bands within the 560–585 $cm^{-1}$ and 290–315 $cm^{-1}$ ranges, as shown in (Scheme 3). These two bands can be assigned to the Ru–O and Ru–Cl stretching modes respectively.
(6) The absorption bands at 3250–3120 $cm^{-1}$ and at ~1625 ± 5 $cm^{-1}$, after complexation, have been assigned to $\nu$(NH) and $\nu$(C═N) respectively.

## $^1$H NMR spectra of the uncomplexed polymers

The $^1$H NMR spectra of the uncomplexed polymer $HL_n$ exhibit a signal at $\delta$ 3.61 ppm. This signal disappears upon addition of $D_2O$. This signal is attributed to the proton of the CH group and suggests that the uncomplexed polymer exists mainly in the azo form (Scheme 2, Fig. 2). The signals in the 6.2–8.9 ppm region are due to the aromatic protons (Table 4). El-Sonbati *et al.*[22] investigated the NMR spectra of $HL_n$ with $UO_2$(II) salts in which the disappearance of the CH (~3.61 ppm) signal with the simultaneous appearance of a new signal in the 11.6–11.2 ppm region is attributed to the proton of the NH group, i.e. with a change from azo to hydrazone form. The spectrum of $HL_3$ showed the expected peaks and pattern of the vinyl group ($CH_2$═CH), i.e. $\delta$(DMSO-$d_6$) 6.23 (dd, $J = 17$, 11 Hz) for the vinyl CH proton and proton $\delta$ 5.09 ppm (AM part of AMX system dd, $J = 17$, 1 Hz and dd, $J = 11$, 1 Hz) for the vinyl $CH_2$ protons. These peaks disappeared upon polymerization and a triplet at $\delta$ 1.76 (t, $J = 7$ Hz) appeared. This indicates that the polymerization of $HL_3$ occurs on the vinyl group.[18,19] It is worth noting that the rest of the proton spectra of the monomer and polymer remain almost without change.

## Reaction of $[Ru(HL_n)Cl_3]_n$ with diamine

The condensation reaction of 3-[(4-derivatives phenyl)diazenyl]-1-(vinyloxy)pentene-2,4-dione ($HL_n$) ruthenium polymer complex with malonyl dihydrazine in ethanol–DMF in the presence of sodium acetate gives macrocyclic ruthenium polymer complexes (Scheme 4).

The IR spectra of the macrocylic ruthenium complexes show few significant changes compared with the products. The $\nu$(CO) band disappears. Only one band is observed in the $\nu$(NH) region at ~3235 $cm^{-1}$, which may be due to a secondary amine group establishing the condensation of the primary amino group with $[Ru(HL_n)Cl_3]$. This is further supported by the appearance of a very weak band at ~1618 $cm^{-1}$ in the new $[Ru(HL'_n)Cl_3]$ macrocyclic polymer complexes, establishing

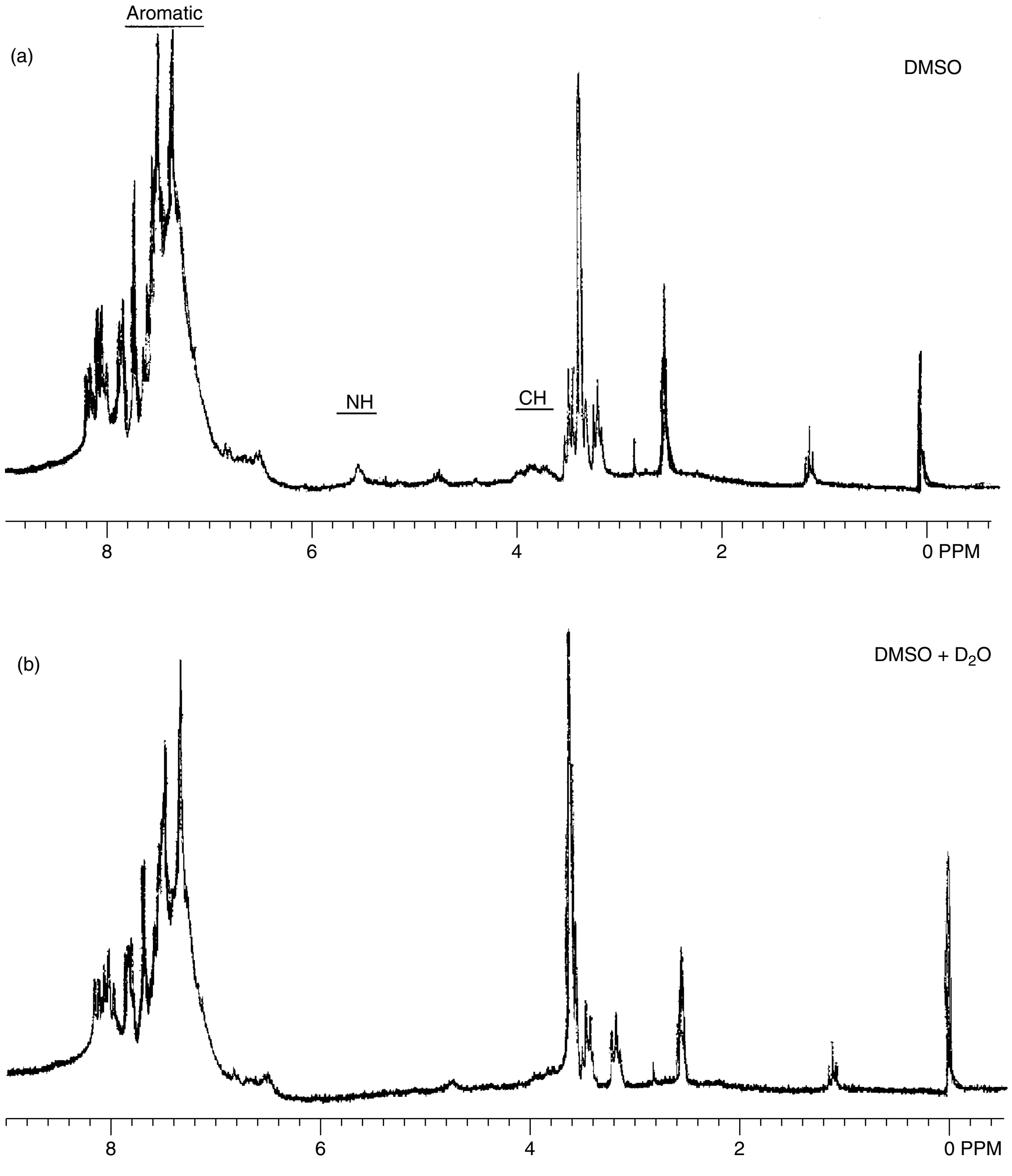


**Figure 2.** $^1$HNMR spectra of $HL_3$ in (a) DMSO-$d_6$ and (b) with $D_2O$.

the formation of an azomethine linkage (Table 1), which is attributed to a C=N stretching mode of the newly formed azomethine linkage. These macrocyclic polymer complexes **6**–**10** show one band at ~1685 cm$^{-1}$ due to the C=O moiety in the ligand amide group. No other bands attributable to $\nu$(C=O) of the allyl-$\beta$-diketone moiety are observed above 1635 cm$^{-1}$. This clearly indicates the presence of two terminal hydrazinic amino groups of the diamine, which give rise to formation of a cyclic molecule (Scheme 4).

In all the present polymer complexes, the bands with medium and weak intensity in the IR region ~305–325 cm$^{-1}$, $\nu$(Ru–Cl),[21] indicate the presence of a terminal coordinated chloride ion[23] and also confirm the octahedral (**A** and **1**–**5**) and trigonal bipyramidal (**6**–**10**) stereochemistry of the ligands around the ruthenium ion.

## CONCLUSIONS

From the overall studies presented, $HL_n$ behaves as a chelating neutral ligand, bonding through two oxygen atoms. $HL_n$ was characterized by analytical and spectral methods before using it for the preparation of the polymer complexes.

The reaction of [RuHL$_n$Cl$_3$], as a neutral ligand, with diamine in ethanol–DMF in the presence of $CH_3COONa$ leads to six-membered ring macrocyclic polymer complexes [Ru(HL$'_n$)Cl$_3$]. The resulting macrocycle retains an N=C bond whose low electrophilic character prevents its reduction by the hydride.

The ligands have several isomers, and these are probably involved in coordination towards metal ions. To verify the stability of the possible structures of the coordination compounds prepared, one can assume that there are two different types of behaviour for coordination compounds. In the first type, the ligand coordinates as a chelate through two carbonyl oxygen atoms as a bidentate ligand. The second type of coordination behaviour was bidentate through two nitrogen atoms of the azomethine groups. The good agreement between calculated and experimental data supports the assignment of the first type suggested in the present work. It is of interest to compare these results with earlier findings. The fact that a definite abscence of the N=N and the appearance of the NH and C=N bands implied the presence of the latter bands after complexation. The bands were cited as evidence for the formation of the hydrazone system (Fig. 2) in the ruthenium polymer and macrocyclic polymer complexes.

Analytical data for the ruthenium polymer complexes are in good agreement for 1 : 1 stoichiometry. The data also indicate the presence of chloride molecules. In conclusion, the results arising from the present investigations confirm that the selected 3-[(4-derivatives phenyl)diazenyl]-1-(vinyloxy)pentane-2,4-dione (HL$_n$) ligands are suitable for building a supramolecular structure. Moreover, since the azo and/or hydrazo compounds experience photochemical isomerization and are, therefore, of interest for applicative purposes,[24] the ruthenium(III) macrocyclic polymer complexes containing the 3-[(4-derivatives phenyl)diazenyl]-1-(vinyloxy)pentane-2,4-dione (HL$_n$) moiety are considered promising supramolecules that could be useful in molecular materials. Work is under way on the synthesis and characterization of further ruthenium, rhodium, uranyl and vanadyl polymer compounds of this family of ligands with a view towards the development of such molecular materials.

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