Infrared and Resonance Raman Spectroscopic Characterization of Electronically Conducting Ruthenium(II) Co-ordination Polymers

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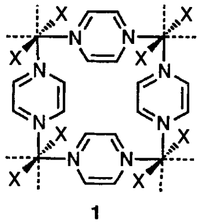
Resonance Raman spectra are presented for a series of ruthenium(II) co-ordination polymers $[\{Ru(L\text{–}L)_xCl_2(dmso)_{4-2x}\}_n]$ [L–L = pyrazine (pyz), *p*-phenylenediamine (ppd) or 1,4-diisocyanobenzene (dib); dmso = dimethyl sulphoxide; $x = 1$ or 2], obtained from the reaction between $[RuCl_2(dmso)_4]$ and L–L in toluene. When an excess of ligand is used samples of formula $[\{Ru(L\text{–}L)_3Cl_2(dmso)\}_n]$ are isolated. There is intensity enhancement of the bands assigned to totally symmetric vibrations of the bridging ligand, resulting from the uniquely strong metal-to-ligand charge transfer bands of the Ru^{II} complexes. While pyz and ppd are N-donors, with Ru–N stretching bands at 274 and 280 cm^{-1} respectively, the more unusual bidentate ligand dib is a C-donor with a Ru–C stretching band at 186 cm^{-1}. The mode of co-ordination is apparent from the IR and Raman spectra: when x is close to 1 the polymers contain bridging ligands but when $x = 3$, the polymers contain terminal ligands. Structures involving one-dimensional chains and two-dimensional grids with bridging L–L are proposed.

There is currently considerable interest in co-ordination polymers on account of their unusual physical properties.[1] For example, doping $[\{Ru(pc)(dib)\}_n]$ (pc = phthalocyaninate dianion, dib = 1,4-diisocyanobenzene) with iodine[2] raises its electrical conductivity by four orders of magnitude. Some of the polymers of type $[\{MX_2(pyz)_2\}_n]$ (M = Co,[3] Ni,[3] Fe[4,5] or Cu;[6,7] X = halide and pyz = pyrazine) have strong magnetic coupling between the metal centres.[8] The coupling is transmitted over the pyrazine ligands which bridge between the metal centres in a two-dimensional grid as in structure **1**. Alternatively, in some cases the halide ions may be bridging with the pyrazines as terminal ligands as in the corresponding pyridine polymers (structure **2**). The rhodium polymer $[\{Rh(dib)\}_n]Cl_n$ is also believed to have a two-dimensional grid as in **1**, but with square planar, rather than octahedral, co-ordination around the metal.[9] Other polymers of formulae $[\{MX_2(pyz)_n]$ [where X is a bidentate anion and M = $Cu^{6,10-12}$ or Zn^{13} (structure **3**), or X = halide and M = Fe^5 or Co^{14} (proposed structure **4**)] and $[\{AgX(pyz)\}_n]$ (structure **5**)[15] are known where each has a one-dimensional chain of bridging ligands. Meyer and co-workers[16] have reported a method of synthesising cationic chains of Creutz–Taube-like Ru complexes with pyz as the bridging ligand. Recently, we reported the synthesis and enhanced electrical conductivity on doping a series of Ru^{II} co-ordination polymers formed in the reaction between $[RuCl_2(dmso)_4]$ (dmso = dimethyl sulphoxide) and L–L [L–L = pyz, *p*-phenylenediamine (ppd) or dib] in toluene.[17] The empirical stoichiometry of the polymers is $Ru(L\text{–}L)_xCl_2(dmso)_{4-2x}$ where $x = 1$ for L–L = pyz or dib, and $x = 1.5$ for L–L = dib or ppd. The formulae suggest bidentate bridging L–L in a one- or two-dimensional polymer. We have provided X-ray powder diffraction evidence for a tetragonal structure based on a two-dimensional grid. In the presence of excess of L–L, a compound of formula $[Ru(L\text{–}L)_3Cl_2(dmso)]$ (L–L = pyz or ppd) is isolated. In the present study we use resonance Raman (RR) spectroscopy to confirm the proposed structure and also to explore the structural and electronic changes after doping with iodine. We believe that RR spectroscopy is a particularly useful technique for probing the structures of these polymers.



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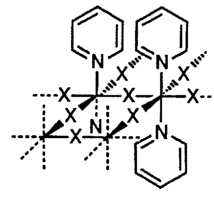

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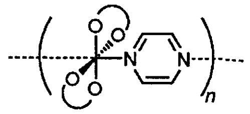

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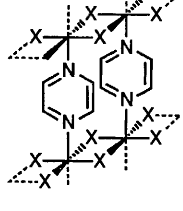

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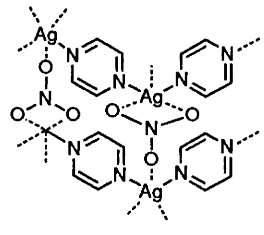

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Experimental

Ruthenium(III) chloride hydrate (Johnson Matthey), pyrazine (Lancaster) and 1,4-diaminobenzene (Aldrich) were used without any further purification. 1,4-Diisocyanobenzene was prepared by a literature method.[18] The complex $[RuCl_2(dmso)_4]$ was prepared by refluxing $RuCl_3{\cdot}xH_2O$ (2.21 g) in dmso for 0.5 h. The orange–brown solution was left to cool and the yellow crystalline solid was filtered off, washed with dmso

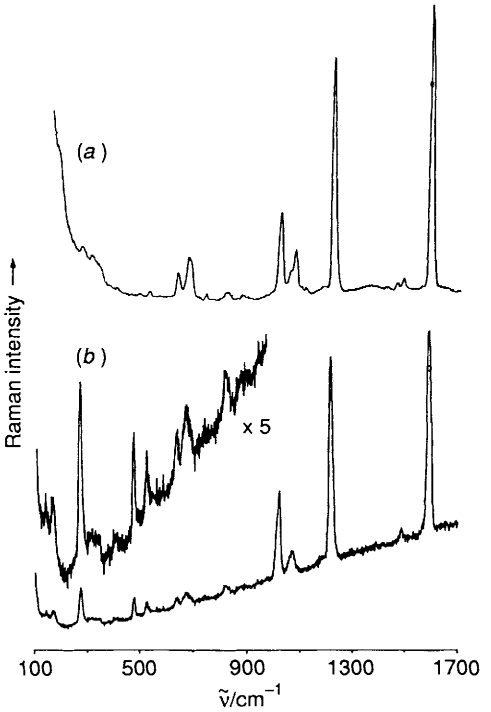


Fig. 1 Raman spectrum of the polymer of $[\{Ru(pyz)_3Cl_2(dmso)\}_n]$ as a KBr disc; λ_0 = 457.9 (*a*) and 619.3 nm (*b*), 1 scan, integration time 1 s

and dried *in vacuo*.[19] All polymers were synthesised in the same way, but with differing ratios of ligand to $[RuCl_2(dmso)_4]$. The reactions were generally carried out under N_2 in refluxing toluene or CH_2Cl_2. The polymer products formed as precipitates which were filtered off, washed and dried. Ruthenium analyses were determined spectrophotometrically.[20] In both series of polymers, $[\{Ru(L\text{–}L)_xCl_2(dmso)_{4-x}\}_n]$ and $[\{Ru(L\text{–}L)_3Cl_2(dmso)\}_n]$, small deviations from the ideal stoichiometry were evident from microanalysis data. Nevertheless the analyses were all consistent with the general formula $Ru(L\text{–}L)_xCl_2(dmso)_{4-2x}$. It is not yet known whether these deviations reflect changes in the chain length of the polymers or the presence of mixtures of polymers. It should be noted that complete substitution of the dmso ligands does not occur. The resistance of the final dmso ligand to substitution has been observed previously.[19]

Conductivity measurements were obtained from 13 mm pressed discs, prepared under a pressure of 15 kbar (1.5 × 10^9 Pa) for 1–2 min. The conductivity apparatus was based on the four-point probe technique.[21]

Resonance Raman spectra were obtained from samples dispersed in KBr discs, mounted either in a liquid nitrogen-cooled cell, or a rotating sample holder for room-temperature measurements. The spectra were recorded on a Spex 1403 spectrometer interfaced to a DMIB computer, using excitation from a Coherent Radiation Innova 90-6 argon-ion laser and 590 dye-laser with 4-dicyanomethylene-6-(*p*-dimethylaminostyryl)-2-methyl-4*H*-pyran as the laser dye. All spectra were obtained with the laser power maintained at < 100 mW at the sample, multi-scanned to improve the signal-to-noise ratio, and corrected for the spectral response of the instrument. Wavenumber calibration of the spectrometer was established by reference to the emission spectrum of neon. The spectral slit width varied from 1 cm^{-1} at 619.3 nm to 3 cm^{-1} at 457.9 nm wavelength excitation.

Infrared spectra of KBr discs were recorded on either a Perkin-Elmer 1440 dispersive spectrometer or a Perkin-Elmer 1710 FTIR spectrometer. Electronic absorption spectra were recorded on a Perkin-Elmer Lambda 5 spectrophotometer.

Results and Discussion

(*a*) *Pyrazine Polymer* $[\{Ru(pyz)_3Cl_2(dmso)\}_n]$.—The RR spectrum of $[\{Ru(pyz)_3Cl_2(dmso)\}_n]$ [Fig. 1(*b*)] obtained with 619.3 nm excitation, close to the maximum of a metal-to-ligand charge-transfer (m.l.c.t.) absorption band,[22] can be interpreted by reference to the bands of the pyrazine ligand (Table 1). In the *A*-term RR scattering regime[23] only bands attributed to totally symmetric vibrations are enhanced (Table 2). Clark and Stead[28] showed that for Ru^{II}–pyridine complexes, excitation within the contour of the $b_2(\pi^*) \longleftarrow b_2(d_{yz})$ m.l.c.t. band at 545–640 nm leads to enhancement of the a_1 vibrations of the pyridine ring. Prominent bands in the polymer spectrum at 1592, 1216, 1020 and 674 cm^{-1} are close to the following bands in the spectrum of pyrazine:[24,25] 1578 (ν_{8a}), 1230 (ν_{9a}), 1013 (ν_1) and 596 (ν_{6a}) cm^{-1}. The positions and relative intensities of these bands are very similar to those of $[\{MCl_2(pyz)_2\}_n]$ (M = Co or Ni), which has a sheet-like structure **1**,[29] and to the Creutz–Taube ion.[26,27] In the latter the Ru–N(pyz) stretching vibration is located at 328 cm^{-1}, while in $[(NH_3)_5Ru^{II}(pyz)Cu^{II}]$ it is found at 318 cm^{-1}.[22] The ν(Ru–N) band for $[\{Ru(pyz)_3Cl_2(dmso)\}_n]$ is observed at 274 cm^{-1}, which is rather lower than for complexes with monodentate pyrazine because the Ru is bound to two pyrazine ligands. This band cannot be assigned to a terminal ν(Ru–Cl) vibration which would be expected at higher wavenumber. Neither can it be attributed to a bridging ν(Ru–Cl) mode which would be expected at much lower wavenumber. A band at 480 cm^{-1} corresponds to the most co-ordination sensitive band of pyrazine, the b_{2u} mode which occurs at 417 cm^{-1} in the free ligands.[30] A band at 312 cm^{-1} in the IR spectrum is assigned to ν_{asym}(Ru–Cl) by analogy with *cis*- and *trans*-$[RuCl_2(py)_4]$ (py = pyridine) complexes,[31,32] although we cannot determine unambiguously whether the $RuCl_2$ group in the polymer is *cis* or *trans*.

The RR spectrum is very similar when excited at 457.9 nm [Fig. 1(*a*)], although the band at 480 cm^{-1}, assigned to the b_{2u} pyrazine internal mode, is much less intense than for 619.3 nm excitation. Additional bands appear at 1461 and 744 cm^{-1}, while the bands at 636, 677 and 1076 cm^{-1} are more intense. These bands are assigned tentatively to dmso vibrations which are enhanced by m.l.c.t. (L = dmso) excitation. The ν(SO) stretch at 1074 cm^{-1} is shifted considerably from that of the free ligand, at 1055 cm^{-1}, which is typical for S-bonded dmso complexes. The bands at 677 and 636 cm^{-1} are assigned to ν(CS).

Doping the polymer with iodine has very little effect on the RR spectrum, indicating that there are no significant structural changes on iodination. It is noted that the band at 636 cm^{-1} is much reduced in intensity in the 457.9 nm spectrum, and that the bands at 480 and 528 cm^{-1} are less intense in the 619.3 nm spectrum.

(*b*) *Pyrazine Polymer* $[\{Ru(pyz)Cl_2(dmso)_2\}_n]$.—By using a lower pyrazine-to-Ru ratio (2:1) in the synthesis, a yellow-brown powder with empirical formula $[Ru(pyz)Cl_2(dmso)_2]$ can be isolated. Laser-excitation of this sample resulted in intense luminescence and a Raman spectrum could not be obtained. The IR spectrum (Fig. 2) clearly shows the absence of the 1586 cm^{-1} band, characteristic of monodentate pyrazine.[30] Similarly bands at 1410, 1212, 1110, 987, 950, 932, 805, 625, 740, 525, 490 and 315 cm^{-1} were reduced in intensity or absent. The spectrum is thus considerably simplified and more closely resembles that of bidentate or unco-ordinated pyrazine.

(*c*) p-*Phenylenediamine Polymer* $[\{Ru(ppd)_{1.5}Cl_2(dmso)\}_n]$.—This polymer is a pale green crystalline solid whose empirical formula, determined by microanalysis, suggests that there are three ppd ligands, each bound to two different Ru atoms. However, it is noted that the compound first isolated has more ppd ligands per Ru atom (3:1) but these are removed on heating *in vacuo*. It is possible that terminal ppd ligands are present initially and that these transform to bridging ligands in the polymer. Many of the IR bands of this polymer (Table 3)

Table 1 Raman and IR spectra of the polymer $[\{Ru(pyz)_3Cl_2(dmso)\}_n]$

$\tilde{\nu}$/cm^{-1}			$\tilde{\nu}$/cm^{-1}		
Raman	IR	Assignment	Raman	IR	Assignment
	3435			994	a_u
	3100	b_{1u}, b_{3u}		938	
	3021	b_{2g}	824w		
	2922	dmso		811	b_{2u}
	2361			744	b_{1g}
	1636	H_2O		717	ν(CS), dmso
1592vs	1583	a_g	674w	680	ν(CS), dmso
	1509	b_{2g}	640w	631	
1486w	1479	b_{1u}	528w	533	
	1460	b_{1u}	480w	496	b_{2u}
	1417	b_{3u}		427	ν(RuS) or δ_{sym}(CSO)
	1311	$\delta(CH_3)$, dmso		380w	
1216vs	1220	a_g		342w	ν_{asym}(RuCl)
	1160	b_{1u}		312m	
	1115	b_{2g}	274m		ν(RuN)
1070w		b_{1u}		230	
1020m	1016	a_g	170w		
			134w		

Table 2 Wavenumbers (cm^{-1}) of the totally symmetric vibrational modes of pyrazine and of Ru–pyrazine complexes

Band	pyz[a]	$Ru^{II,II}$ dimer[b]	$Ru^{II,III}$ dimer[b]	$Ru^{III,III}$ dimer[b]	$[\{Ru(pyz)_3Cl_2(dmso)\}_n]$[c]
ν_2	1578	1593	1596	1621	1592
ν_3	1230	1224	—	1253	1216
ν_4	1015	1084	1070	1055, 1033[d]	1020
ν_5	596	689	701	692	528
ν(MN)	—	326	328	350	274

[a] Refs. 24 and 25. [b] Refs. 26 and 27; $[(NH_3)_5Ru(pyz)Ru(NH_3)_5]^{n+}$ where n = 4, 5 or 6. [c] This work. [d] Fermi resonance gives rise to two ν_4 bands.[26,27]

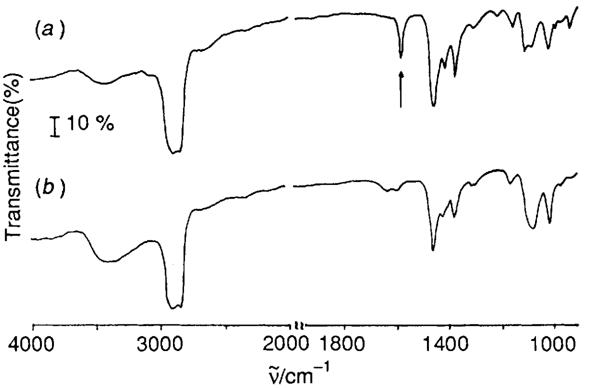


Fig. 2 IR spectra of (*a*) $[\{Ru(pyz)_3Cl_2(dmso)\}_n]$ and (*b*) $[\{Ru(pyz)Cl_2(dmso)_2\}_n]$ as KBr discs. The arrow indicates the symmetric pyrazine stretching mode at 1583 cm^{-1}

can be readily assigned to ppd vibrations by comparison with literature values.[33] There are some differences in the relative band intensities, presumably due to the lowering of symmetry on co-ordination. Other bands are assigned to the dmso ligand by comparison with the spectrum of $[RuCl_2(dmso)_4]$.[20] The ν(NH) region contains several overlapping sharp bands. A comparison of the Raman data with those of the free ligand[33] reveals some major differences (Fig. 3, Table 4). In particular bands at 1500 and 1257 cm^{-1} in the spectrum of ppd are not observed in the polymer spectrum, while prominent bands are observed at 1456, 1402 and 1142 cm^{-1} for the polymer. One possible explanation is suggested by the similarities of the spectra of the oxidised ligand ppd$^+$ and Ru polymer (Table 4). The band at 1091 cm^{-1} is attributed to ν(S=O) of S-bonded dmso, which is at higher wavenumber than in the free molecule (1055 cm^{-1}), and two strong bands at 682 and 690 cm^{-1} are assigned to ν(CS). The low-wavenumber region is complex, making it difficult to assign the skeletal modes of the polymer. In the IR spectrum ν(RuCl) is observed at 318 cm^{-1} and an intense band near 280 cm^{-1} may be assigned to ν(RuN), consistent with that observed for the Ru–pz adduct.

The ppd complex is slightly soluble in dimethylformamide giving a pale yellow–green solution [λ_{max} = 450, 540(sh) and 625(sh) nm]. Under N_2 the 540 nm band decreases in intensity and the 625 nm band grows (isosbestic point at 555 nm), during which time the solution becomes deep green. In CH_2Cl_2 the band positions are at 450, 570 and 625(sh) nm. On standing in air for 20 min this solution becomes intense purple (λ_{max} = 540 nm). By comparison with spectroscopic data obtained by Ludi and co-workers from monomeric[34] and dimeric[35] *p*-benzoquinone diimine derivatives the bands above 500 nm may be assigned to m.l.c.t. absorptions. The IR spectrum of the blue powder extracted from the CH_2Cl_2 solution by addition of ether contains a strong band at 1507 cm^{-1} indicating that some terminally bonded ppd is still present.

On doping with iodine the bands due to the ppd ligand in the Raman spectrum are much weaker. This is to be expected if Ru^{II} has been oxidised to Ru^{III} and the m.l.c.t. absorption is removed. A strong band at 680 cm^{-1} may be assigned to ν(CS) of the dmso ligand. Other strong bands occur at 319 cm^{-1}, assigned to ν(RuCl), and 557 cm^{-1}. The IR spectrum is not altered substantially on oxidation except for the appearance of a sharp band at 1385 cm^{-1} and the coalescence of the ν(NH) bands. The electrical conductivity of the polymer increases dramatically from 2×10^{-11} to 3×10^{-3} S cm^{-1} on exposure to iodine vapour whereas the conductivities of the other polymers only increase by three orders of magnitude on doping with iodine. This may be due to the fact that the bridging ligand can be oxidised to the quinone diimine in the ppd complex. A broad absorption band above 3000 cm^{-1} appears in the IR spectrum of the doped polymer. The band at 1502 cm^{-1} assigned to a symmetric ring mode in the untreated complex disappears, indicating that loss of terminal ligands occurs and a different ring mode appears at

Table 3 Raman and IR spectra of the polymer $[\{Ru(ppd)_{1.5}Cl_2(dmso)\}_n]$

$\tilde{\nu}/cm^{-1}$ Raman	$\tilde{\nu}/cm^{-1}$ IR	Assignment	$\tilde{\nu}/cm^{-1}$ Raman	$\tilde{\nu}/cm^{-1}$ IR	Assignment
	3413m		1010m	1009s	
	3323s			977m	
	3287m			942w	
	3254s		922w	921w	
	3096m		848w	845m	ring br
	3015m		825w	829m	
	2919m	ν(CH), dmso		722m	ν(CS), dmso
1612m	1615m	ν(ring)	690w	679m	
1596(sh)			682(sh)		
	1566m	δ(NH), ν(ring)		550m	
	1517vs			539m	
1456w	1455m	ν(CN)		447m	
1402m	1408m		415vw	425w	δ(CSO), dmso
	1308w			385w	ν(RuCl)
	1280m			320w	
1234w	1231w		283w		ν(RuN)
1173w	1178m	δ_{op}(CH), ppd	200w		
1142m	1135m		172w		
1091w			150(sh)		
1055w	1062vs	ν(SO), dmso	142w		
	1025s				

op = Out of plane, br = breathing.

Table 4 Wavenumbers (cm^{-1}) of the main *p*-phenylenediamine (ppd) bands in the Raman spectra of ppd, ppd^+ and the Ru–ppd polymer

ppd[a]	ppd^{+}[a]	$[\{Ru(ppd)_{1.5}Cl_2(dmso)\}_n]$[b]	Assignment
1631	1648	1612	ν(ring)
1500	—	—	
1257	1428	1456, 1402	ν(CN)
1130	1186	1142	δ_{op}(CH)
		283	ν(RuN)

[a] Ref. 33. [b] This work.

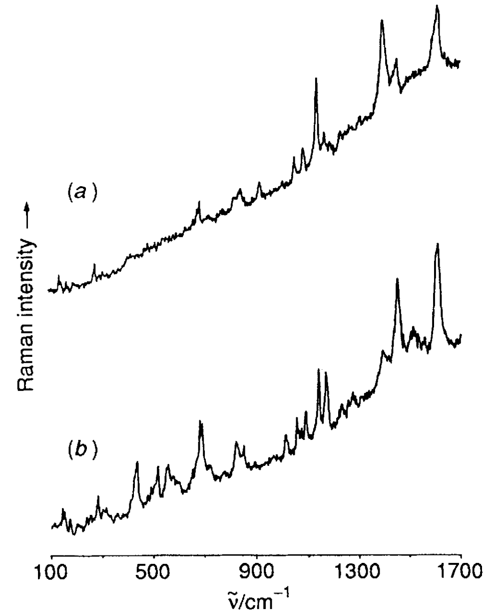


Fig. 3 Raman spectrum of the polymer $[\{Ru(ppd)_{1.5}Cl_2(dmso)\}_n]$ as a KBr disc at 80 K; λ_o = 457.9 (*a*) and 514.5 nm (*b*), 2 scans, integration time 1 s

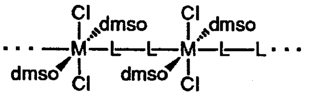
1578 cm^{-1} while ν(CN) bands at 1255 and 1275 cm^{-1} disappear, with a new band appearing at 1384 cm^{-1}. This may reflect the change in CN bond order on oxidation; in the free-ligand radical cation ν(CN) shifts to 1423 cm^{-1}.[33] It should be noted that the spectrum of the doped polymer does not in any way resemble that of poly(1,4-diaminobenzene).[36]

(*d*) 1,4-*Diisocyanobenzene Polymer* $[\{Ru(dib)_{1.5}Cl_2(dmso)\}_n]$.—As for the pyrazine polymer the Raman spectrum is rather simple, although in this case it is overlapped by a strong luminescence background (Fig. 4). There is the same apparent enhancement of a_1 bands and the lack of correspondence with the IR spectrum (Table 5). Once again, dmso bands are observed at 646 and 708 cm^{-1}. The band due to ν(NC) appears at 2127 cm^{-1}, which is very close to the free ligand value of 2130 cm^{-1}.[37] In contrast to the other polymers a strong band at 186 cm^{-1} is observed. This is assigned tentatively to ν(RuC). It could possibly be due to bridging Ru–Cl although we consider this unlikely since terminal ν(RuCl) bands are observed at 344 cm^{-1} in the IR spectrum.

On doping with iodine there is a large increase in the luminescence background in the Raman spectrum and, as for the other polymers, resonance enhancement is lost upon oxidation. Weak shoulders at 165 and 200 cm^{-1} may be assigned tentatively to I_n^- species.

Conclusion

For the pyz and dib polymers both the internal bridging-ligand modes and the skeletal-mode region confirm that the ligands L–L are bidentate in a polymeric structure. The dmso ligands



may be replaced by monodentate L–L ligands if an excess of the latter is present. The single ν(RuCl) band in the Raman spectrum confirms the *trans*-$RuCl_2$ arrangement.

Iodine doping of the pyz and dib polymers does not alter the

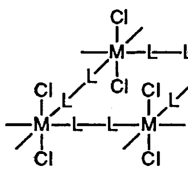


Table 5 Raman and IR spectra of the polymer $[\{Ru(dib)_{1.5}Cl_2(dmso)\}_n]$

$\tilde{\nu}$/cm^{-1}		
Raman	IR	Assignment
3094w		ν(CH)
	3002w	
	2917w	
2127	2136vs	ν(CN)
2095vw		
	1685w	
1602vs	1602m	ν(ring)
	1509m	
	1417w	
1312vw	1312m	δ(CH), dmso
1194m	1197w	
1170vs	1165m	δ_{op}(CH)
1156(sh)		
	1103m	
	1019m	
	975w	
	952w	
825m	839m	δ_{ip}(CH)
807m		
	731m	
708m	700m	
646m	647m	dmso
502vw	514m	
449m		
436vw	429m	
	382w	δ(CSO), dmso
	344w	ν(RuCl)
186vs		ν(RuC)

ip = In plane.

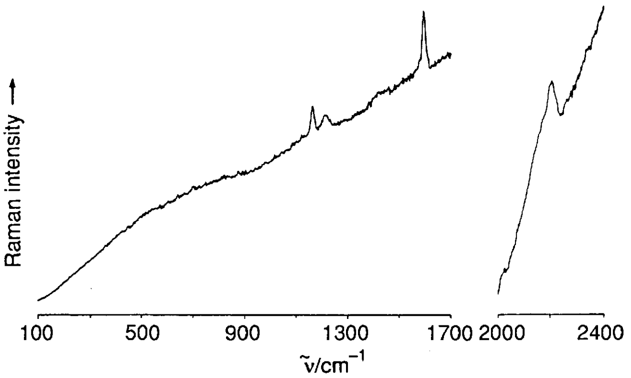


Fig. 4 Raman spectrum of the polymer $[\{Ru(dib)_{1.5}Cl_2(dmso)\}_n]$ as a KBr disc; λ_0 = 457.9 nm, 9 scans (100–1700 cm^{-1}), 20 scans (2000–2400 cm^{-1}), integration time 1 s

spectra greatly apart from introducing bands due to I_n^- species. The spectrum of the ppd polymer can also be analysed in terms of this structure but the number of bands is much larger, possibly due to the lack of selective resonance enhancement, or to a more flexible binding mode of this ligand. Iodine uptake by this polymer leads to enhanced conductivity but the Raman spectrum is changed radically, with possible break-up of the polymer chains.

When x approaches 2, the polymer may contain a two-dimensional grid structure, consistent with our X-ray powder diffraction data. This type of structure has been observed in $[\{Rh(dib)_2\}_n]Cl_n$[9] and $[\{CoCl_2(pyz)_2\}_n]$.[3] When $x = 2$ some of these grid patterns may be broken up resulting in terminal L–L moieties.

As a result of this work we now have a much improved understanding of the structures of these materials. Further studies are in progress to devise rational synthetic routes to polymers in which all the dmso ligands have been replaced, and to crystallise these substances in order to obtain X-ray data to establish the structures proposed.

Acknowledgements

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