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Spectroscopic and electrochemical studies of a series of copper(I) and rhenium(I) complexes with substituted dipyrido[3,2-*a*:2′,3′-*c*]-phenazine ligands†

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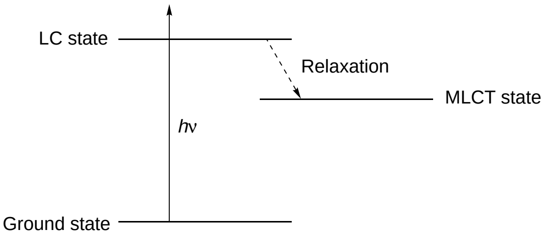
Copper(I) and rhenium(I) complexes with the ligand dipyrido[3,2,-*a*:2′,3′-*c*]phenazine (dppz) and a number of substituted analogues have been synthesized. Their spectroscopic and electrochemical properties have been studied. It is found that the lowest-energy transition for the complexes is metal-to-ligand charge transfer (MLCT) in nature. This has a low ε value. The resonance Raman spectra for the complexes show groups of bands that shift with substitution at the ligand and groups that remain unchanged in wavenumber. Electrochemical reduction of the complexes resulted in the formation of the ligand radical anion species for all but one system. This was confirmed by UV/VIS spectroelectrochemistry. Using resonance Raman spectroelectrochemistry marker bands have been identified for the radical anion species. The excited states of the complexes were studied by excited-state electronic absorption and time-resolved resonance Raman techniques. The former spectra are ambiguous as to the nature of the lowest excited state; however, the latter spectra confirm that this state is ligand-centred for complexes of dppz and its 11-methyl derivative. Complexes with the 11-nitro derivative appear to form excited states that are MLCT in nature.

Metal complexes with ligands based on dipyrido[3,2-*a*:2′,3′-*c*]-phenazine (dppz) are of interest because of their interactions with DNA,[1] their molecular switching properties[2] and their potential in solar energy conversion schemes.[3] In most solar energy conversion schemes, based on transition-metal complexes, solar energy is captured through a charge-separation scheme, such as excitation to the metal-to-ligand charge-transfer, MLCT, state.[4] The advantage of using dppz-based systems in such schemes is that the overlap between the metal d_π and ligand π^* orbitals is small,[5] thus reducing the back electron-transfer rate. However the poor overlap between these orbitals results in a very low oscillator strength for the MLCT transition reducing the efficiency of directly forming the charge-separated state. A possible solution to this is to use the strongly allowed ligand-centred, LC, transitions of the complex to sensitize the formation of the charge-separated MLCT state as depicted in Scheme 1. For this strategy to be successful the LC states must have a large ε in the solar spectral region, the lowest excited state must be MLCT in nature and the photophysics of the complex must lead to population of the MLCT state.



Scheme 1

The excited-state properties of complexes with dppz as a ligand have been studied by a number of groups. The nature of the lowest excited state for these systems falls into two categories: (1) for complexes containing ruthenium(II) and osmium(II) evidence from excited-state absorption, electronic emission and time-resolved resonance Raman spectroscopies suggests a lowest excited state of MLCT character;[6] (2) for rhenium(I) complexes with dppz the nature of the lowest excited state is somewhat ambiguous. Schanze and co-workers[7] have shown that $[Re(CO)_3(dppz)(Mepy)]^+$ (where Mepy is 4-methylpyridine) has an LC lowest excited state. The emission spectrum from this complex shows vibrational structure characteristic of such states. A detailed analysis of the quenching properties of the complex revealed the presence of an MLCT state lying close in energy to the lowest LC state. Time-resolved infrared spectroscopy has been used to probe the nature of the lowest excited state of $[Re(CO)_3(dppz)(PPh_3)]^+$.[8] The infrared spectrum provided definitive evidence for an LC lowest excited state. Furthermore the same paper reports that the emission spectrum of $[Re(CO)_3(dppz)(PPh_3)]^+$ and the corresponding chloro complex appears to be of MLCT origin at room temperature.

In the foregoing studies it is clear that for rhenium(I) complexes with dppz the LC and MLCT states lie very close in energy. Our study seeks to use substitution at the dppz ligand to alter the levels of the LC and MLCT states. In this regard the properties of a number of copper(I) and rhenium(I) complexes with substituted dipyrido[3,2-*a*:2′,3′-*c*]phenazine ligands have been investigated. The advantages of using such complexes are as follows. (i) The $Cu(PPh_3)_2^+$ and $Re(CO)_3Cl$ moieties do not possess chromophores in the visible region, thus the spectroscopy of the complexes is more readily interpreted. (ii) Copper(I) and rhenium(I) offer interesting contrasts in photophysical behaviour. The excited-state properties of copper(I) complexes are strongly affected by the substituent groups on the ligands used.[9] For rhenium(I) systems the photophysical properties, such as excited-state lifetime, depend more on the energy-gap law than on steric effects.[10] (iii) The metal moieties have different π-acid properties perturbing the ligand to differing extents when complexed.

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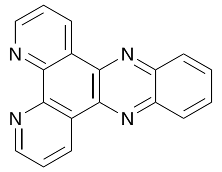
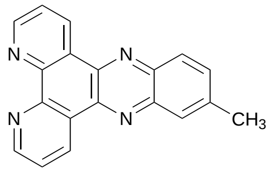
† *Supplementary data available*: electronic and resonance Raman spectra. For direct access see http://www.rsc.org/suppdata/dt/1998/609, otherwise available from BLDSC (No. SUP 57350, 8pp) or the RSC Library. See Instructions for Authors, 1998, Issue 1 (http://www.rsc.org/dalton).

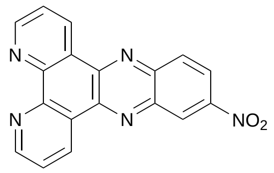
The substituents on the dipyrido[3,2-*a*:2′,3′-*c*]phenazine ligands are electron-withdrawing NO_2 and Cl groups or electron-donating methyl groups.



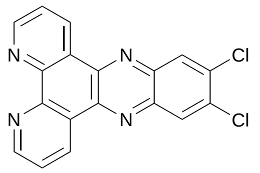
L^1



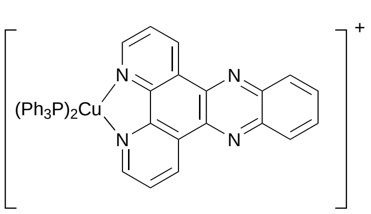
L^2



L^3



L^4



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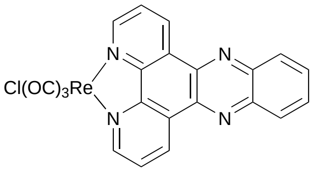

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Experimental

Materials

The compounds [$Re_2(CO)_{10}$], 1,10-phenanthroline, *o*-phenylenediamine, 2,3-diaminotoluene, 1,2-diamino-3-nitrobenzene and 1,2-diamino-4,5-dichlorobenzene were obtained commercially and used without further purification. The complex [Cu(PPh$_3$)$_2$(MeCN)$_2$]BF$_4$ was prepared by the reaction of [Cu(MeCN)$_4$]BF$_4$ with 2 equivalents of PPh$_3$ in acetonitrile solution,[11] [Re(CO)$_5$Cl] from [$Re_2(CO)_{10}$] by the method of Schmidt *et al.*[12] For electrochemical and spectroscopic measurements solvents of spectroscopic grade were used. These were further purified by distillation and stored over 5 Å molecular sieves. The supporting electrolytes used in the electrochemical measurements were tetrabutylammonium perchlorate and hexafluorophosphate. These were further purified by repeated recrystallizations from ethanol–water and ethyl acetate–diethyl ether respectively.[13]

Ligand synthesis

Ligands were prepared by the Schiff-base condensation of 1,10-phenanthroline-5,6-dione with the appropriate diamino compound in ethanol under reflux. The best yields were obtained if the diamino compound was present in *ca.* 20% excess.[14] The dione was prepared by oxidation of 1,10-phenanthroline following the method of Gillard *et al.*[15]

L^1: δ_H(200 MHz, solvent CDCl$_3$, standard SiMe$_4$) 9.65 (2 H, dd), 9.28 (2 H, dt), 8.36 (2 H, dd), 7.93 (2 H, dd) and 7.80 (2 H, dd) (Found: C, 76.21; H, 3.69; N, 19.51. Calc.: C, 76.58; H, 3.57; N, 19.85%); yield 40%.

L^2: δ_H(200 MHz, solvent CDCl$_3$, standard SiMe$_4$) 9.59 (2 H, dt), 9.25 (2 H, dt), 8.21 (1 H, d), 8.08 (1 H, s), 7.76 (3 H, m) and 2.70 (3 H, s) (Found: C, 77.29; H, 3.95; N, 19.12. Calc.: C, 77.01; H, 4.08; N, 18.91%); yield 55%.

L^3: δ_H(200 MHz, solvent CDCl$_3$, standard SiMe$_4$) 9.54 (2 H, m), 9.30 (2 H, m), 9.20 (1 H, d), 8.64 (1 H, dd), 8.44 (1 H, d) and 7.80 (2 H, m) (Found: C, 65.73; H, 2.98; N, 21.28. Calc.: C, 66.05; H, 2.77; N, 21.40%); yield 48%.

L^4: δ_H(200 MHz, solvent CDCl$_3$, standard SiMe$_4$) 9.48 (2 H, dd), 9.28 (2 H, dd), 8.42 (2 H, s) and 7.77 (2 H, dd) (Found: C, 61.34; H, 2.06; N, 15.77. Calc.: C, 61.56; H, 2.30; N, 15.95%); yield 56%.

Synthesis of complexes

Copper(I) complexes were formed by the reaction of [Cu(PPh$_3$)$_2$(MeCN)$_2$]BF$_4$ with the appropriate ligand in dichloromethane solution under an argon atmosphere. The reactions proceeded rapidly at room temperature forming the coloured complex within seconds of mixing the two reagents. The complexes were purified by recrystallization from methanol: [CuL^1(PPh$_3$)$_2$]BF$_4$ **1** (Found: C, 68.07; H, 4.60; N, 5.51. Calc.: C, 67.74; H, 4.21; N, 5.85%), yield 70%; [CuL^2(PPh$_3$)$_2$]BF$_4$ **2** (Found: C, 67.79; H, 4.23; N, 6.11. Calc.: C, 68.00; H, 4.36; N, 5.76%), yield 76%; [CuL^3(PPh$_3$)$_2$]BF$_4$ **3** (Found: C, 64.35; H, 4.03; N, 7.36. Calc.: C, 64.71; H, 3.92; N, 6.99%), yield 73%; [CuL^4(PPh$_3$)$_2$]BF$_4$ **4** (Found: C, 62.86; H, 3.88; N, 5.29. Calc.: C, 63.13; H, 3.73; N, 5.45%), yield 60%.

The rhenium complexes were formed by the addition of [Re(CO)$_5$Cl] to a solution of appropriate ligand in dry methanol under reflux conditions. The reacting mixture was kept under an argon atmosphere for *ca.* 8 h. At this time it was pale yellow and contained the complex as an orange-yellow precipitate. This was filtered off while hot and washed with ether. It was found that if the mixture was allowed to cool residual ligand would coprecipitate with the complex.

[ReL^1(CO)$_3$Cl] **5**: δ_H(200 MHz, solvent CDCl$_3$, standard SiMe$_4$) 9.87 (2 H, dd), 9.47 (2 H, dd), 8.46 (2 H, dd) and 8.04 (4 H, m) (Found: C, 42.84; H, 1.54; N, 9.67. Calc.: C, 42.90; H, 1.71; N, 9.53%); yield 78%.

[ReL^2(CO)$_3$Cl] **6**: δ_H(200 MHz, solvent CDCl$_3$, standard SiMe$_4$) 9.82 (2 H, dt), 9.45 (2 H, dt), 8.32 (1 H, d), 8.20 (1 H, s), 8.00 (2 H, dd), 7.88 (1 H, dd) and 2.64 (3 H, s) (Found: C, 43.71; H, 1.80; N, 9.29. Calc.: C, 43.89; H, 1.84; N, 9.31%); yield 72%.

[ReL^3(CO)$_3$Cl] **7**: δ_H(200 MHz, solvent CDCl$_3$, standard SiMe$_4$) 9.86 (2 H, dd), 9.52 (2 H, dd), 9.38 (1 H, d), 8.80 (1 H, dd), 8.63 (1 H, d) and 8.09 (2 H, m) (Found: C, 39.73; H, 1.10; N, 11.37. Calc.: C, 39.84; H, 1.34; N, 11.07%); yield 84%.

[ReL^4(CO)$_3$Cl] **8**: δ_H(200 MHz, solvent CDCl$_3$, standard SiMe$_4$) 9.79 (2 H, dd), 9.48 (2 H, dd), 8.60 (2 H, s) and 8.04 (2 H, dd) (Found: C, 38.41; H, 1.06; N, 8.83. Calc.: C, 38.40; H, 1.23; N, 8.53%); yield 75%.

Physical measurements

A Perkin-Elmer Lambda-19 spectrophotometer was used for collection of electronic absorption spectra. This was calibrated with a Ho_2O_3 filter and spectra were run with a 2 nm resolution. Cyclic voltammograms were obtained from argon-purged degassed solutions of compound (*ca.* 1 mM) with 0.1 M concentration of NBu_4ClO_4 or NBu_4PF_6 present. The electrochemical cell consisted of a 1.6 mm diameter platinum working electrode embedded in a Kel-F cylinder with a platinum auxiliary electrode and a saturated potassium chloride calomel reference electrode. The potential of the cell was controlled by an EG&G PAR 273A potentiostat with model 270 software. The NMR spectra were recorded using a Varian 200 MHz spectrometer.

Raman scattering was generated using continuous wave (Spectra-Physics model 166 argon ion) and nanosecond pulsed (Continuum Nd:YAG Surelite I-10) lasers. The sample was held in a spinning NMR tube, or optically transparent thin-layer electrode (OTTLE) cell, and the scattering collected in a

135° backscattering geometry. The irradiated volume was imaged into a Spex 750M spectrograph using a two-lens arrangement.[16] The spectrograph was equipped with an 1800 g mm^{-1} holographic grating which provided a dispersion of 0.73 nm mm^{-1}. The Raman photons were detected using a Princeton Instruments liquid-nitrogen-cooled 1152-EUV charge-coupled detector (CCD) controlled by a Princeton Instruments ST-130 controller; CSMA v2.4 software (Princeton Instruments) was used to control the CCD and spectra were analysed and prepared for presentation using GRAMS/32 (Galactic Industries Corp.) software. Spectral windows were approximately 18 nm wide and were calibrated using emission lines from a neon lamp or from an argon-ion laser. The calibrations were checked by measuring the Raman band wavenumber positions for a known solvent.[17] For the data reported herein the calibrations were accurate to *ca.* 1 cm^{-1}. Rayleigh and Mie scattering from the sample were attenuated using a Notch filter (Kaiser Optical Systems Inc.) of appropriate wavelength. A polarization scrambler was placed in front of the spectrograph entrance slit. A 150 μm slit width was used on the spectrograph and this gave a resolution of *ca.* 6 cm^{-1} with 450 nm excitation.

For the time-resolved resonance Raman measurements 448.3 nm was employed as an excitation wavelength. This was generated by stimulated Raman scattering[18] through acetonitrile, contained in a 10 cm cell, using the 354.7 nm third harmonic of the Nd:YAG pulsed laser. It was found that with 50 mJ per pulse of 354.7 nm light, 3.5 mJ per pulse of 448.3 nm was obtained. The pulse energy of the 448.3 nm beam was attenuated by lowering the 354.7 nm pump energy.

The electronic absorption spectra of reduced species were measured using an OTTLE cell with a platinum grid as the working electrode.[19] For Raman spectra of reduced species a similar cell was employed. Initial measurements found that the signal-to-noise ratios of the Raman spectra were reduced because of reflection off the platinum grid. This problem was alleviated by removing a portion of the centre of the grid (*ca.* 2 × 4 mm) and aligning the laser to irradiate the solution in that region.

Excited-state absorption (ESA) difference spectra were measured using apparatus described previously.[20]

Results

The compounds are readily soluble in organic solvents. They appear stable in solution for prolonged periods. The rhenium(I) complexes are less soluble than their copper(I) counterparts but are also stable in solution.

Electrochemical data for the ligands, copper(I) and rhenium(I) complexes in dichloromethane are presented in Table 1. The methyl group has little effect on the position of the first reduction potential in the metal complexes. However, copper(I) and rhenium(I) complexes with electron-withdrawing ligands L^3 and L^4 are more readily reduced relative to the complexes with ligand L^1. The pattern of shifts in reduction potential with substitution is unsurprising in that the electron-withdrawing groups shift $E^{\circ\prime}$ to more positive values. Binding of the ligands to copper(I) has almost no effect on the $E^{\circ\prime}$ values, however the rhenium complexes are easier to reduce than the ligands alone. The differences observed between differing rhenium complexes is similar to that observed between the corresponding free phenazines. Therefore the reductions are assigned as ligand based.

The electronic absorption data for the ligands and complexes are presented in Table 2. The absorption spectra of the ligands show $\pi^* \longleftarrow \pi$ transitions in the 370 nm region. Stronger ligand-centred transitions are observed at wavelengths shorter than 300 nm. The electronic spectra of the complexes show visible absorptions tailing out to 400–500 nm. These visible shoulders extend further into the red with complexes which are easier to reduce.

The Raman spectra of the ligands, L^1–L^3, are complicated by strong emission signals even at excitation wavelengths in the red, *i.e.* 632.8 nm. It is possible to observe the surface-enhanced Raman scattering (SERS) by measuring the scattering from a roughened silver electrode.[22] The SERS spectra of L^1–L^4 are shown in Fig. 1 (band positions are in Table 3) with the resonance Raman spectrum of L^4 in CH_2Cl_2, generated at 363.8 nm. The SERS spectra are similar, showing strong bands at about 1580 and 1600 cm^{-1}. The resonance Raman spectrum of L^4 shows a number of bands at similar wavenumbers to those of the SERS spectrum, however the strong features at 1600 cm^{-1} are absent. This suggests that these features are enhanced through interaction with the silver electrode surface. The wavenumbers of observed bands in the spectra of the ligands and complexes are listed in Table 3. The resonance Raman spectra of the rhenium(I) complexes are shown in Fig. 2.

Table 1 Electrochemical data for ligands and complexes

Compound	$E^{\circ\prime}$ [a]/V	Compound	$E^{\circ\prime}$ [a]/V
L^1	−1.28	L^3	−1.05
L^2	−1.30	L^4	−0.93
1	−1.25	**5**	−1.01
2[b]	−1.31	**6**	−1.04
3	−1.04	**7**	−0.95
4	−0.93	**8**	−0.83

[a] Reduction potentials are given *versus* SCE. Solvent used CH_2Cl_2, supporting electrolyte NBu_4ClO_4 or NBu_4PF_6. All waves are fully reversible, unless indicated, showing a ratio of currents for the anodic and cathodic peaks of unity and peak separation between anodic and cathodic waves of *ca.* 60 mV.[21] [b] Does not show reversible electrochemistry.

Table 2 Electronic absorption data for ligands and complexes and their reduced species

	λ_{max}/nm (CH_2Cl_2)* ($10^{-4} \times \varepsilon$/M^{-1} cm^{-1})	
Compound	Parent species	Reduced species
L^1	270 (4.37), 367 (1.13), 379 (1.29)	267 (3.84), 361 (1.08), 487 (0.494), 569 (0.245)
L^2	273 (4.70), 365 (1.05), 385 (1.22)	263 (3.08), 297 (2.21), 364 (0.635), 484 (0.223)
L^3	297 (4.31), 306 (3.84), 371 (1.61), 389 (1.31)	297 (4.31), 358 (1.68), 387 (sh), 413 (sh), 483 (0.75), 513 (0.59)
L^4	272 (5.39), 370 (1.54), 391 (2.13)	264 (2.65), 374 (0.632), 483 (0.257)
1	277 (5.5), 364 (0.86)	270 (3.8), 335 (1.31), 587 (0.45)
2	281 (8.35), 369 (1.64)	272 (7.85), 365 (1.12), 384 (1.32)
3	285 (6.35), 368 (1.90), 386 (1.45) (sh)	267 (4.43), 355 (2.58), 405 (1.48), 488 (1.23), 520 (1.13), 802 (0.717)
4	278 (12.0), 369 (2.50), 388 (2.74)	266 (7.97), 335 (3.75), 370 (1.96), 391 (2.01), 609 (1.06)
5	280 (5.00), 360 (1.38)	258 (3.51), 297 (2.79), 336 (2.18), 584 (0.945)
6	285 (9.71), 324 (2.03) (sh), 371 (2.01), 387 (2.05)	260 (5.10), 297 (3.87), 347 (3.58), 601 (1.38)
7	285 (5.67), 296 (5.66), 320 (1.84) (sh), 359 (1.63)	284 (3.78), 357 (2.85), 406 (1.50), 491 (1.11), 523 (1.09)
8	283 (9.97), 322 (2.07) (sh), 370 (2.36), 375 (2.38), 389 (2.21)	260 (5.74), 294 (3.88), 338 (4.27), 394 (2.00), 458 (0.920), 604 (1.61)

* Except for L^2 (MeOH).

The changes in the electronic absorption spectra of compounds L^1–L^4 through electrochemical reduction are presented in Table 2. The electrochemical reduction of L^1 to (L^1)$^-$ has been reported by Kaim and co-workers.[23] They observed the bleach of the ground-state features at 379 and 359 nm with new bands at 572, 545 and 450 nm upon reduction. The spectrum of (L^1)$^-$ generated in CH_2Cl_2 differs somewhat in terms of band intensities from that reported by Kaim. However we obtained identical spectral changes to those reported when using dmf as solvent. For L^1–L^4 the changes in the spectra with reduction have well defined isosbestic points. The electronic spectra of the reduced ligands show visible absorptions that are assigned as $\pi^* \longleftarrow \pi$ transitions of the radical anion. The presence of long-wavelength absorptions is characteristic of radical anion polypyridyl ligands.[24]

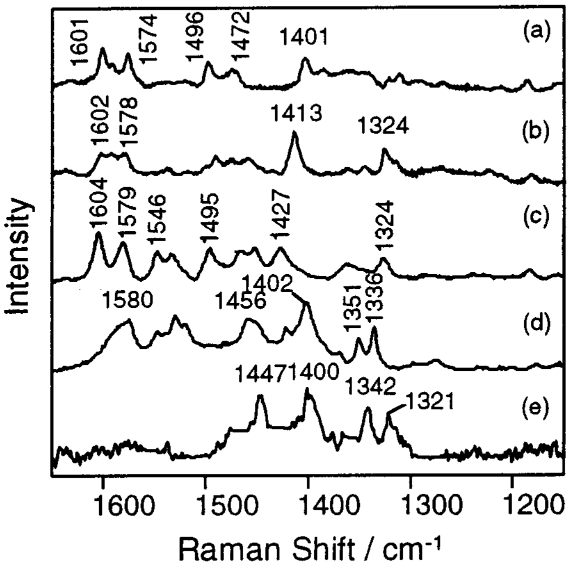

Fig. 1 Raman spectra of ligands: (a) L^1, (b) L^2, (c) L^3, (d) L^4. λ_{exc} = 514.5 nm, 20 mW. Scattering measured from the surface of a roughened silver electrode in methanolic solution (for L^1–L^3), CH_2Cl_2 solution for L^4. (e) L^4, λ_{exc} = 363.8 nm, 8 mW, CH_2Cl_2 solution

The wavelengths of the absorption bands observed in the reduced species of complexes **1**–**8**, are presented in Table 2. Well defined isosbestic points are observed for each reduction, indicating the conversion from one species into another, or a number of other species with minimum side reactions. For all complexes except **2** the observed changes are fully reversible. The electronic spectra of all the reduced complexes except **2**$^-$ show absorption features similar to those of the corresponding reduced ligands. For **2** application of a potential to a solution of the complex gives a species with an electronic spectrum identical to that of free L^2. This strongly suggests that the reduction of **2** is occurring at the copper(I) site, thus leading to demetallation of the complex. Such electrochemistry is very common among copper(I) systems,[25] indeed the behaviour of the other copper complexes, **1**, **3** and **4** is unusual in that they show reduction at the ligand.[26]

Strong emission from the reduced products of L^1–L^4 makes it impossible to measure the resonance Raman spectra for these species. However, it is possible to observe the surface-enhanced

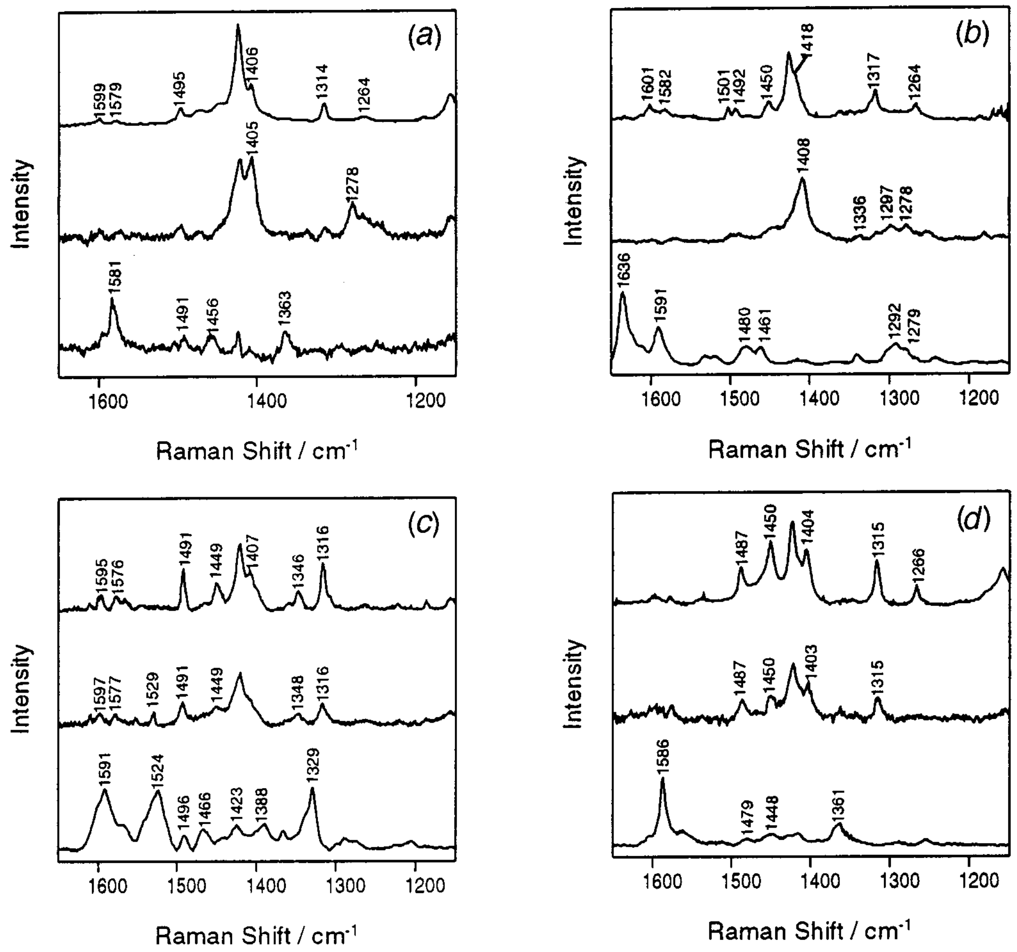

Fig. 2 Upper trace: ground-state resonance Raman spectrum in CH_2Cl_2 solution (1 mM), λ_{exc} = 457.9 nm continuous wave, laser power 20 mW for complexes **5** (*a*), **6** (*b*), **7** (*c*) and **8** (*d*). Middle trace: corresponding time-resolved resonance Raman spectrum, λ_{exc} = 448.3 nm pulsed excitation, laser energy 3 mJ per pulse. Lower trace: resonance Raman spectrum of electrochemically reduced **5** (*a*) or **8** (*d*) in CH_2Cl_2 solution (1 mM), λ_{exc} = 514.5 nm continuous wave, laser power 20 mW; or surface-enhanced resonance Raman spectrum of ligand L^2 (*b*) or L^3 (*c*) in methanol reduced at roughened silver electrode, λ_{exc} = 514.5 nm, 20 mW

Table 3 Wavenumbers (cm^{-1}) of bands observed in Raman spectra for ligands and complexes

L^{1a}	L^{2a}	L^{3a}	L^{4b}	L^{4c}	**1**^{d}	**2**^{d}	**3**^{d}	**4**^{d}	**5**^{d}	**6**^{d}	**7**^{d}	**8**^{d}
1601s	1602	1604	1580 (br)		1614w	1613vw		1592w	1599w	1601w	1595w	
1574s	1578	1579			1597w	1594vw			1579w	1582w	1576w	
		1546				1503vw				1501w		
1496s		1495			1495m	1487vw		1477m	1495m	1492w	1491s	1487m
1472					1468m	1443m	1443m	1446s		1450m	1449m	1450s
			1456	1447	1443m	1412s	1408m	1401s	1406s	1418s	1407m	1404s
		1427			1402m							
1401	1413s		1402s	1400s								
	1324m	1324w	1351w	1342			1333s				1346w	
			1336m	1321	1315s	1316s	1317m	1316s	1314s	1317s	1316s	1315s
									1264w	1264m		1266m

[a] The SERS spectrum in methanolic solution. [b] The SERS spectrum in CH_2Cl_2 solution. [c] λ_{exc} = 363.8 nm, 8 mW, CH_2Cl_2 solution. [d] λ_{exc} = 457.9 nm, 20 mW, CH_2Cl_2 solution. s = Strong, m = medium, w = weak, v = very, br = broad.

Table 4 Wavenumbers (cm^{-1}) for bands observed in the resonance Raman spectra of reduced ligands and complexes

(L^1)$^{-a}$	(L^2)$^{-a}$	(L^3)$^{-a}$	(L^4)$^{-a}$	**5**$^{-b}$	**8**$^{-b}$
1633s	1636s				
1589m	1592m	1591s	1584s	1581s	1586s
1520w	1532m	1524s			
1480w	1518m	1496w	1505m	1491w	1479w
1462w	1481m	1466w	1453w	1456w	1448w
	1462m	1423w			
1389w	1340w	1388w		1363m	1361m
1302m		1329s			
1264m	1293m				

[a] The SERRS spectrum in methanol reduced at roughened silver electrode. λ_{exc} = 514.5 nm, 20 mW. [b] Resonance Raman spectrum in CH_2Cl_2 solution. λ_{exc} = 514.5 nm, 20 mW.

resonance Raman scattering (SERRS) of the reduced ligands at a roughened silver electrode. The wavenumbers for bands observed in the SERRS spectra of (L^1)$^-$–(L^4)$^-$ are given in Table 4. The spectra of (L^1)$^-$ and (L^2)$^-$ are similar in the high-wavenumber region, *i.e.* around 1600 cm^{-1}. The spectrum of (L^3)$^-$ is significantly different with no 1630 cm^{-1} feature. This may be caused by the nitro group interacting with the surface of the roughened electrode. Such interactions are well known for silver and gold electrode surfaces.[27] This normally results in increased enhancement of Raman scattering for the nitro vibration, relative to other vibrations of the molecule, and small shifts in the wavenumber of the band, relative to scattering from a bulk sample. It is possible to generate the spectra of **5**$^-$ and **8**$^-$ in solution [Fig. 2(*a*) and 2(*d*)] due to the low emission from these species. Band positions are listed in Table 4.

The wavenumbers of bands observed in the resonance Raman spectra using 448 nm pulsed excitation for complexes **1**–**3** and **5**–**7** are listed in Table 5. No excited-state features are observed in the time-resolved spectra of **4** or **8**. The 448 nm excitation is in resonance with electronic transitions of the ground and excited state for all of the complexes. Thus it is possible to generate the time-resolved resonance Raman spectra of the excited states using the single-colour pump-probe protocol.[28]

The resonance Raman spectra for the rhenium complexes with 448 nm pulsed excitation are shown in Fig. 2. Resonance Raman scattering generated with 448 nm pulsed excitation for **5** shows similar bands to the ground-state spectrum generated with 457.9 nm excitation. However, a number of important differences are observed: (i) the ground-state band at 1314 cm^{-1} is almost completely bleached in the pulsed spectrum; (ii) a new band at 1278 cm^{-1} is observed in the pulsed spectrum, assigned to the excited state of **5**. Fig. 2(*b*) shows the time-resolved spectrum of **6**. This differs from the ground-state resonance Raman spectrum in a number of ways: ground-state features at 1264, 1317, 1582 and 1601 cm^{-1} are absent from the pulsed spectrum and that at 1418 cm^{-1} appears shifted to 1408 cm^{-1}. New features at 1278 and 1297 cm^{-1} appear in the pulsed spectrum. Fig. 2(*c*) shows the time-resolved spectrum of **7**. The pulsed spectrum shows one feature (1529 cm^{-1}) not observed in the ground-state spectrum generated at 457.9 nm.

Table 5 Wavenumbers (cm^{-1}) for bands observed in the time-resolved resonance Raman spectra of complexes in CH_2Cl_2 solution

1	**2**	**3**	**5**	**6**	**7**
1592w		1591m			1597vw
					1577vw
					1529w
1493w		1486m	1495vw		
1441m	1441m	1440s			1491m
1403s	1410s	1408m	1405s	1408s	1449m
1357m		1345m		1336vw	1348w
1316m	1318m	1315s		1297w	1316s
1277w			1278m	1278w	

The pulsed spectrum for complex **8** has no new features compared to the ground state. As the pulse energy is increased the ground-state bands diminish relative to the solvent feature at 1423 cm^{-1}.

Discussion

The majority of studies of complexes with dppz and related ligands have focused on the interaction of the systems with DNA.[1] A number of studies have examined the detailed spectroscopic properties of the complexes.[5,23] This study represents an examination of the spectroscopic, electrochemical and excited-state properties of a series of complexes in which the ligand is altered by substitution with electron-donating and -withdrawing groups.

A number of questions concerning the use of such ligands need to be addressed. (i) How does binding to the metal alter the ground-state properties? (ii) How do the complexes behave when reduced, *i.e.* their spectroelectrochemistry? This is an important point because it provides spectral information on the ligand-radical anion species which is present in the MLCT excited state. (iii) How do the complexes behave when photoexcited?

Ground-state properties

Theoretical treatments of compound L^1 suggest that the dppz ligand has three MOs which lie close in energy:[23] (i) the lowest-lying MO is termed b_1(phz), and is localized on the phenazine (phz) portion of the ligand; (ii) the $b_1(\psi)$[29] orbital, localized at the 2,2′-bipyridine (bpy) portion of the ligand; (iii) the $a_2(\chi)$ orbital also localized at the bpy portion of the ligand.[29] These calculations show that the amplitude of the wavefunction for the LUMO [b_1(phz)] is very small at the chelating nitrogens. Thus the oscillator strength and ε for the MLCT transitions of complexes with L^1 would be expected to be small. The electronic spectra of **1**–**8** show weak absorptions tailing to 450–500 nm depending on the complex. The ε for these features are *ca.* 1000 M^{-1} cm^{-1}. The absorptions extend further into the red in complexes with electron-withdrawing ligands such as L^3. Furthermore, the rhenium(I) complexes absorb further into the red than do the copper(I) counterparts. They are also easier to reduce suggesting the π* ligand acceptor orbital is at lower energy. These patterns of behaviour are consistent with MLCT transitions.

A number of studies report the resonance Raman spectra of L^1 and its ruthenium(II) complexes.[30] The other ligands and their complexes have not been reported to date. The resonance Raman spectrum of $[Ru(dmb)_2L^1]^{2+}$ (dmb = 4,4′-dimethyl-2,2′-bipyridine), generated using 496.5 nm excitation, has been reported.[6] The following bands were assigned to dppz: 1181, 1304, 1404, 1446, 1469, 1488, 1569 and 1596 cm^{-1}. The resonance Raman spectrum of $[Ru(phen)_2L^1]^{2+}$ (phen = 1,10-phenanthroline), generated using 457.9 nm excitation, showed dppz bands at 1189, 1266, 1311, 1361, 1407, 1475, 1496, 1577 and 1600 cm^{-1}.[29] In the former study the band at 1404 cm^{-1} was described as a dominant feature. In the second study the most prominent features lie at 1475, 1496, 1577 and 1600 cm^{-1}.

The resonance Raman spectra of complexes **1**–**8** differ from those reported for ruthenium complexes in that only the dppz ligand is involved in the resonant chromophore(s). For all of the complexes reported herein the higher wavenumber bands at 1600 cm^{-1} are only weakly enhanced and the strongest Raman bands lie at *ca.* 1400 and at *ca.* 1315 cm^{-1}. The band at *ca.* 1400 cm^{-1} shifts significantly with substitution of the ligand and this behaviour is consistent with assignment to a dominant ring stretch involving the entire ligand framework. The 1315 cm^{-1} band is wavenumber-insensitive to substitution. A phenanthroline-based vibration, such as that proposed by Campos-Valette and co-workers,[31] is consistent with this behaviour. This is a vibration that only involves motion of the atoms bound close to the metal. Complexes containing the nitro group, **3** and **7**, show bands at 1333 and 1346 cm^{-1} respectively. These are assigned as the nitro stretch on the basis of their frequency.[32]

Resonance Raman spectroscopy provides some insight into where an excited electron may be directed in an MLCT transition by virtue of the fact that the modes most strongly enhanced are associated with the resonant chromophore.[33] The strong enhancement of the 1400 cm^{-1} band and the enhancement of the nitro vibration in the spectra of complexes **3** and **7** is consistent with an MLCT from the transition metal to b_1(phz). The strong enhancement of the phen-based mode at 1300 cm^{-1} suggests that an MLCT transition involving the 'bpy-based' MOs may also be resonant at 457.9 nm.

Spectroelectrochemistry

For all of the ligands and complexes, except **2**, reduction is based on the ligand, thus a radical anion is formed. In the case of the ligands the spectra observed shift considerably with substitution, exemplified by those of $(L^3)^-$ and $(L^2)^-$ (Table 2). This is consistent with population of a b_2(phz) MO. On binding to a metal centre there are some small changes in the electronic spectra of the reduced species. The species $(L^3)^-$, $\mathbf{3}^-$ and $\mathbf{7}^-$ all show absorptions at approximately 360, 410, 490 and 520 nm. This suggests the metal has little effect on the MO occupied by the reducing electron in the reduced species.

In attempting to model the Raman spectral signatures of the radical anion species of ligands L^1–L^4 SERRS spectra were collected because conventional Raman spectra were obscured by strong emission from the reduced ligands. The SERRS spectra may be significantly perturbed from solution-phase spectra as evidenced by the SERS and resonance Raman spectra of L^4 (Fig. 2). Different enhancement patterns and wavenumber shifts in band positions may occur depending on the normal modes of vibration of the ligand and the nature of the interaction with the surface.[34] There is therefore a need for caution in relating SERRS spectra to those of species in the solution phase. However, for two of the complexes it was possible to generate a resonance Raman spectrum of the reduced species. These spectra of $\mathbf{5}^-$ and $\mathbf{8}^-$ [Fig. 2(*a*) and 2(*d*)] are similar, showing two prominent bands for the radical anion species. These lie at *ca.* 1362 and 1583 cm^{-1}. For $\mathbf{5}^-$ the 1581 cm^{-1} feature is close to the 1589 cm^{-1} band observed in the SERRS of $(L^1)^-$. A band at 1367 cm^{-1} is also observed in the SERRS spectrum although it is of low intensity. The SERRS spectra for $(L^1)^-$ contain the bands observed for $\mathbf{5}^-$ but at rather different intensities. The strongest band in the SERRS spectrum lies at 1633 cm^{-1} and is presumably due to some surface-binding phenomenon. (The SERS spectrum of 1,10-phenanthroline shows a high-frequency mode at 1625 cm^{-1}. See ref. 34.)

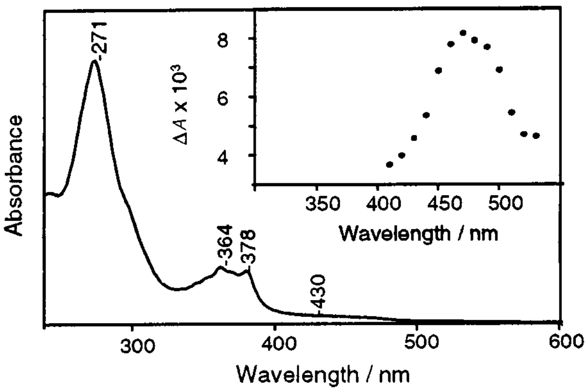

Fig. 3 Electronic absorption spectrum of complex **1** in CH_2Cl_2. Inset: Δ*A* spectrum of transient electronic absorption signals for the excited state of **1** generated by 355 nm pulsed (7 ns duration) excitation

It is clear that the SERRS spectra give only a qualitative signature for the radical anion species. It is pleasing that the spectra of the two reduced complexes are similar as might be expected. The spectra of complex $\mathbf{8}^-$, and the corresponding ligand SERRS spectrum of $(L^4)^-$ both show strong bands at 1586 and 1584 cm^{-1} respectively. These provide spectral marker bands for the radical anion species. Further evidence that these are radical anion features comes from the time-resolved resonance Raman spectra of $[Ru(phen)_2(dppz)]^{2+}$. The lowest excited state for this compound is assigned as an MLCT state in which the dppz is reduced, thus the spectra show features associated with the $dppz^{\bullet -}$ radical anion. Bands are observed at 1575, 1457 and 1366 cm^{-1}, which lie close to the radical anion features identified in our spectrum of $\mathbf{5}^-$.

Excited-state properties

The λ_{max} for the ESA spectra for all systems (Table 6) that could be measured are remarkably similar. A typical spectrum, that of complex **1**, is shown in Fig. 3. The similarity between the spectra suggests that all of the observed excited states are ligand-centred in nature. The dynamics of the excited states are somewhat more ambiguous. The lifetimes of the ligands are long, up to 10 μs, whereas the complexes with these ligands have rather short lifetimes. For L^2 $\tau \approx 2.5$ μs, but for **2** it is 1.7 μs and for **6** it is only 0.34 μs. This suggests that the metal is having a significant perturbation on the excited state. The most striking example of this is with the nitro-ligand, L^3. The lifetime for the ligand excited state is 10 μs, those of the copper and rhenium complexes are *ca.* 6 ns.

The upshot of this is that the ESA spectra alone are insufficient to provide a clear idea as to the nature of the lowest excited state in these systems. Time-resolved resonance Raman spectroscopy offers a more incisive probe of the excited-state

Table 6 Excited-state lifetimes for ligands and complexes in degassed CH_2Cl_2 at room temperature

Compound	$\tau/\mu s$	ESA, λ_{max}/nm
L^1*	3(300)	460
L^2	2.5	465
L^3	10	460
L^4	10	462
1	0.16	460
2	1.7	475
3	<0.006	—
4	n.s.	—
5	0.04	475
6	0.34	470
7	<0.006	—
8	n.s.	—

n.s. = No signal observed.

* Ref. 7 reports a biphasic decay with two components; the lifetime of the stronger signal is 3 μs and that of the second decay is given in parentheses.

nature. The spectra for the complexes with L^1 show distinct bands associated with their respective excited states. The lifetimes of these states are long with respect to the probe laser pulse and, assuming the absorption of the sample is sufficiently high, efficient population of the state should be readily achievable. The spectral signatures observed bear no resemblance to the resonance Raman spectra of the ligand radical anion species $(L^1)^-$, as observed either in the SERRS spectrum of the ligand or the Raman OTTLE spectrum for the rhenium(I) complex, **5**. The simplest explanation for this finding is that the thermally equilibrated excited (THEXI) states for **1** and **5** do not possess any radical anion character and are LC in nature. This finding is consistent with emission temperature studies carried out on **5** by Meyer and co-workers.[6] For the rhenium(I) complex **6** with ligand L^2, the 448 nm pulsed spectrum clearly shows excited-state features not present in the ground-state spectrum. The excited-state features are similar to those observed for complexes with L^1; they do not correspond well with the SERRS spectrum of $(L^2)^-$ or the Raman spectra of the reduced rhenium complexes $\mathbf{5}^-$ and $\mathbf{8}^-$ [Fig. 2(*a*) and 2(*d*)] recorded for related ligands. The time-resolved spectrum strongly suggests that the THEXI state for **6** has no radical anion character and is LC based.

Complexes with the nitro-substituted ligand, L^3, behave differently from the aforementioned. The excited-state resonance Raman spectra of the copper complex **3** shows a feature at 1591 cm^{-1} which is of similar wavenumber to that observed in the SERRS spectrum of $(L^3)^-$. Furthermore a band is observed at 1346 cm^{-1} which is close to that seen in the Raman spectra of the reduced rhenium complexes. The time-resolved data suggest that the THEXI state of **3** has significant radical anion character. The spectra of **7** taken with 448 nm pulsed irradiation show few changes from that of the ground state measured using 457.9 nm excitation [Fig. 2(*c*)]. The lifetime measurements showed **7** to have a lowest excited-state lifetime less than *ca.* 6 ns. It would be extremely difficult to populate completely such a state using the 10 ns pulsed laser in this study although partial population of the state is possible.[35] The 1529 cm^{-1} band observed in the pulsed spectrum may be due to population of the excited state. It is interesting that a band at 1524 cm^{-1} is present in the SERRS spectrum of $(L^3)^-$. The other features that may be expected for $(L^3)^-$ would lie at 1329 and 1591 cm^{-1}, if one assumes a similar spectral signature to that of the MLCT of **3**, unfortunately ground-state bands are present in this region and may obscure transient features. With the ground and transient state present together in the spectrum it is more difficult to interpret what is observed. Furthermore, the need to use high pulse energies to generate the transient spectrum in **7** may lead to non-linear effects which complicate the spectrum.[36]

Conclusion

This is the first study in which the nature of the lowest excited state for copper(I) and rhenium(I) complexes with dppz-type ligands in which substituents on the ligands are changed has been carried out. The presence of electron-withdrawing groups appears to lower the energy of the MLCT state so that it dominates the THEXI state population. Without such groups present the lowest excited state is LC in nature. The determination of the nature of the excited state is not straightforward. Time-resolved vibrational spectroscopy, in this case resonance Raman spectroscopy, appears to be the least ambiguous tool for probing the excited-state nature.

We have found that when the MLCT state is lowest in energy its lifetime is very short. This clearly limits the utility of such complexes in homogeneous photocatalytic systems.[37] However, they may be of use in heterogeneous systems, such as liquid-junction solar cells. In such cells the dye material is known rapidly to photoinject into the semiconductor conduction band[38] thereby permitting dye materials with short lifetimes to operate successfully.

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