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FULL PAPER

Electron withdrawing and electron donating effects of 4,4′-bipyridine substituents on ruthenium mono(bipyridine) complexes

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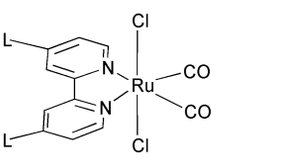
Monobipyridine complexes of ruthenium (4,4′-L_2-2,2′-bpy)Ru$(CO)_2Cl_2$ (L = H, Me, *t*-Bu, Cl, Br, H_2PO_3, NO_2) were synthesised and structurally characterised. The electronic effects of the substituents L on vibration and absorption spectra were studied using both experimental and theoretical methods, calculations were carried out with the density functional hybrid B3PW91 and Hartree–Fock *ab initio* methods. The energy differences between the HOMO and LUMO orbitals of the complexes depended on the electron withdrawing properties of the bipyridine substituents. The electronic effects of the substituents were observed as a correlation between the spectra (λ_{max} and ν_{CO} bands) and the electronic character of the substituents.

Introduction

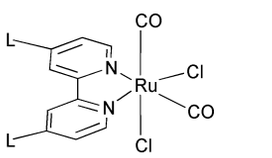
The photo- and electro-chemical properties of the polypyridine-complexes of ruthenium are a widely studied area of organometallic chemistry. Early studies on the photochemical properties of the ruthenium polypyridine complexes have been largely focused on unsubstituted 2,2′-bipyridines.[1] However, the use of different substituents as potential electrochemical and photochemical modifiers has become increasingly important, as a result, for example, of novel photochemical applications such as photosensitised solar cells, where Ru-bipyridine dye is attached to a TiO_2-surface *via* suitable linking carboxylic acid[2] and phosphonic acid[3] groups.

In addition to the acidic groups, alkyl-substituted polypyridine ligands have also been widely used as photo- and electro-chemical modifiers of the ruthenium complexes, and the methyl[3g,4] and *tert*-butyl[5] substituents have been reported to affect the electron transfer and photochemical properties. As electron donors they decrease the Ru(II)/Ru(III) oxidation potential.[3g,5a,6] The photochemical properties (λ_{max} in emission and absorption spectra) analysed by UV-Vis spectrometers have also been reported to be affected by alkyl substituents.[4b,f,g,5a] Similarly, the properties of the ruthenium complexes containing nitro-substituted polypyridine ligands have been reported on.[6b,7]

In the present work, the role of the substituent in the bpy ligand on the photochemical character of the complex was studied. Eight different monobipyridine complexes of Ru containing substituents at the 4,4′-positions were synthesised and their absorption properties were compared. The electronic effects of the substituents on the orbital energies were studied theoretically and the effect on absorption was measured by means of UV-Vis spectroscopic analysis. The infrared spectra for all of the complexes were determined both experimentally and theoretically, and the effect of the ligand system on the carbonyl group vibration was clearly observed. The properties of the complexes containing electron withdrawing groups (Cl, Br, NO_2 and PO_3H_2) were compared with complexes with electron donor substituents (methyl and *tert*-butyl). All of the synthesised complexes are illustrated in Fig. 1



Complex	L
1	H
2	Me
3	*t*-Bu
5	NO_2
6	H_2PO_3
7	Cl
8	Br



Complex	L
4	*t*-Bu

Fig. 1 Synthesised Ru-mono(bipyridines).

Experimental

Materials

The bipyridine complexes of ruthenium Ru(L)$(CO)_2Cl_2$ were synthesised from the bipyridyl ligand L and $[Ru(CO)_3Cl_2]_2$ (Alfa). The reactions were carried out by using commercially purchased ligands: 2,2′-bipyridine (bpy, Aldrich), 4,4′-dimethyl-2,2′-bipyridine (dmbpy, Aldrich) and 4,4′-di-*tert*-butyl-2,2′-bipyridine (Aldrich). Synthesis of the parent ruthenium compound *trans*(Cl)-Ru(bpy)$(CO)_2Cl_2$(**1**)[8] and the dimethyl substituted complex *trans*(Cl)-Ru(dmbpy)$(CO)_2Cl_2$ (**2**)[9] were prepared by the usual methods. The *trans*-chloro isomer of the di-*tert*-butyl substituted complex, *trans*(Cl)-(4,4′-di-*tert*-butyl-2,2′-bipyridine)Ru$(CO)_2Cl_2$ (**3**), was prepared in a similar way to complex **1**, but using the corresponding substituted ligand.

General procedures

All syntheses were carried out air-sensitively under nitrogen and by using deoxygenated solvents. The solid reagents were used without further purification. The FT-IR spectra were measured with a Nicolet Magna-IR 750 spectrometer and the

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NMR spectra with a Bruker Digital NMR Avance 250 MHz spectrometer. Elemental analyses were done with a EA1110 CHNS-O equipment (CE Instruments), and the UV-Vis measurements were carried out using a Perkin-Elmer Lambda 900 UV/VIS/NIR spectrometer.

***cis*(Cl),*cis*(CO)-(4,4′-Di-*tert*-butyl-2,2′-bipyridine)Ru(CO)$_2$Cl$_2$ (4).** 4,4′-Di-*tert*-butyl-2,2′-bipyridine (500 mg, 1.86 mmol) was dissolved in 20 ml ethanol. The solution was transferred by the needle technique into a round-bottomed flask containing 473 mg (0.92 mmol) of [Ru(CO)$_3$Cl$_2$]$_2$ dissolved in ethanol (20 ml). The resulting clear solution was refluxed overnight, yielding a yellow solution. This solution was allowed to cool to room temperature, and finally it was kept at a low temperature (approx. 5 °C) for 30 minutes. A pure yellow product precipitated, which was filtered and washed with cold ethanol. Yield 474 mg (51%). (Found C 48.42; H 5.61; N 5.23. Calc. for $C_{20}H_{26}N_2O_2Cl_2Ru$ C 48.20; H 5.62; N 5.26%). IR (in CH_2Cl_2) ν/cm^{-1} 2064 and 2000 (CO). δ_H (250 MHz, $CDCl_3$) for bpy-ring 9.65 (d, J = 6.0 Hz, 1H), 8.71 (d, J = 6.0 Hz, 1H), 8.10 (s, 2H), 7.70 (d, J = 6.0 Hz, 1H), 7.48 (d, J = 4.5 Hz, 1H) and for *tert*-butyl 2.18 (s, 6H).

***trans*(Cl)-(4,4′-Dinitro-2,2′-bipyridine)Ru(CO)$_2$Cl$_2$ (5).** The dinitro-substituted ligand was synthesised by a method reported in the literature.[10] The ruthenium dimer [Ru(CO)$_3$Cl$_2$]$_2$ was refluxed for 17 h in methanol (205 mg, 0.40 mmol, in 10 ml). The solution of 4,4′-dinitro-2,2′-bipyridine (151 mg, 0.61 mmol, in 5 ml methanol) was added hot to the Ru-solution and the yellow solution was refluxed for 3 h. The yellowish-green precipitate was filtered and washed with methanol and dried in a vacuum. Yield 209 mg (72%). (Found C 30.49; H 1.36; N 11.59. Calc. for $C_{12}H_8N_4O_6Cl_2Ru$ C 30.40; H 1.28; N 11.82%). IR (in CH_2Cl_2) ν/cm^{-1} 2074 and 2018 (CO). δ_H (250 MHz, d^6-acetone) for bpy-ring 9.82 (s, 2H), 9.75 (d, J = 6.0 Hz, 2H), 8.68 (d, J = 5.0 Hz, 2H).

***trans*(Cl)-(4,4′-Diphosphonic acid-2,2′-bipyridine)Ru(CO)$_2$Cl$_2$ (6).** The bipyridine ligand (4,4′-bisphosphonato)-2,2′-bipyridine was prepared according to a literature method.[11] The metal precursor [Ru(CO)$_3$Cl$_2$]$_2$ was refluxed for 17 h in methanol (226 mg, 0.44 mmol, in 15 ml) and added to a suspension of 4,4′-diphosphonic acid-2,2′-bipyridine (240 mg, 0.76 mmol, in 10 ml methanol). The mixture was refluxed for 40 h and a clear orange solution was formed. Methanol was removed by vacuum, resulting in orange product. Yield 256 mg (62%). (Found C 23.70; H 2.18; N 4.48. Calc. for $C_{12}H_{10}N_2P_2O_8Cl_2Ru\cdot 3\frac{1}{2}H_2O$ C 23.82; H 2.50; N 4.63%). IR (in MeOH) ν/cm^{-1} 2074 and 2011 (CO). δ_H (250 MHz, d^4-MeOH) for bpy-ring 9.33 (s, 2H), 8.44 (d, J = 13.5 Hz, 2H), 8.06 (d, J = 12.3 Hz, 2H).

***trans*(Cl)-(4,4′-Dichloro-2,2′-bipyridine)Ru(CO)$_2$Cl$_2$ (7).** A methanol solution of [Ru(CO)$_3$Cl$_2$]$_2$ (201 mg, 0.39 mmol, in 7 ml) was heated under reflux for 18 h. 137 mg (0.61 mmol) of 4,4′-dichloro-2,2′-bipyridine ligand was suspended in methanol (5 ml) and the suspension was added to the Ru solution. The yellow solution was refluxed for 3 h and the precipitate was filtered after cooling. Yield 145 mg (53%). (Found C 31.68; H 1.32; N 6.13. Calc. for $C_{12}H_6N_2O_2Cl_4Ru$ C 31.81; H 1.33; N 6.18%). IR (in CH_2Cl_2) ν/cm^{-1} 2068 and 2007 (CO). δ_H (250 MHz, $CDCl_3$) for bpy-ring 9.19 (s, 2H), 9.08 (d, J = 6.0 Hz, 2H), 7.71 (d, J = 6.3 Hz, 2H). NOTE: A reaction at room temperature using extra ligand (molar ratio bpy : Ru 3 : 2) was carried out without any pre-refluxing of the Ru source. This method resulted in the formation of (4,4′-dichloro-2,2′-bipyridine)Ru(CO)$_2$Cl(C(O)OCH$_3$) (**7b**). Yield 52 mg (38%). (Found C 34.85; H 2.12; N 5.75. Calc. for $C_{14}H_9N_2O_4Cl_3Ru$ C 35.28; H 1.90; N 5.88%). IR (in CH_2Cl_2) ν/cm^{-1} 2060 and 1998 (CO). δ_H (250 MHz, $CDCl_3$) for bpy-ring 8.83 (d, J = 5.8 Hz, 2H), 8.15 (s, 2H), 7.59 (d, J = 5.9 Hz, 2H), and for (–O–CH$_3$) 3.43 (s, 3H).

***trans*(Cl)-(4,4′-Dibromo-2,2′-bipyridine)Ru(CO)$_2$Cl$_2$ (8).** An ethanol solution of 4,4′-dibromo-2,2′-bipyridine (100 mg, 0.32 mmol, in 20 ml) was added to an ethanol solution of [Ru(CO)$_3$Cl$_2$]$_2$ (82 mg, 0.16 mmol, in 20 ml). The mixture was refluxed for 3 h and the orange solution was then allowed to cool to ambient temperature. Compound **8** precipitated as a yellow product. The product was filtered and washed with cold methanol. Yield 95 mg (55%). (Found C 26.74; H 1.15; N 5.19. Calc. for $C_{12}H_6N_2O_2Cl_2Br_2Ru$ C 26.60; H 1.12; N 5.17%). IR (in CH_2Cl_2) ν/cm^{-1} 2068 and 2008 (CO). δ_H (250 MHz, d^4-MeOH) 8.97 (d, J = 6.0 Hz, 2H), 8.34 (s, 2H), 7.85 (d, J = 6.0 Hz, 2H).

X-Ray crystallography

The X-ray diffraction data were collected with a Nonius KappaCCD diffractometer using Mo-Kα radiation (λ = 0.71073 Å) with a Collect[12] data collection program. The Denzo and Scalepack[13] programs were used for cell refinements and data reduction. The structures **3**, **4**, and **5** and **7b** were solved by direct methods using the SHELXS97 program[14] and the WinGX[15] graphical user interface. Structure **6** was solved by the Patterson method using the DIRDIF-99 program.[16] A multi-scan absorption correction based on equivalent reflections (XPREP in SHELXTL v. 5.1)[17] was applied to **4** and **6** (T_{max}/T_{min} were 0.26723/0.23630 and 0.26242/0.19479 respectively). Structural refinements were carried out with the SHELXL97 program.[18] The hydrogens in **3**, **4**, **5** and **7b** and the aromatic hydrogens in **6** were placed in idealised positions and constrained to ride on their parent atom. The data for **6** were not good enough for either hydroxyl hydrogens or the water hydrogens from the difference Fourier map to be located. These hydrogens were placed in calculated positions using the HYDROGEN (CALC-OH)[19] program as incorporated in the WinGX program package. In **6** there were two Ru molecules and seven water molecules in the asymmetric unit.

Structure **5** was solved as a racemic twin (absolute structure parameter 0.51(2)) in the orthorhombic space group *Fdd*2. In **3** chlorines of a solvent molecule CH_2Cl_2 and the methyl groups of one of the *tert*-butyl substituent were disordered in two positions. In **4** chlorines of the solvent molecule $CHCl_3$ were completely disordered around the carbon atom. The hydrogens of the disordered solvents were omitted from both **3** and **4**. The crystallographic data are summarised in Table 1, and selected bond lengths and angles, together with the values for the optimised structures are shown in Table 2. The crystal structures of the complexes **3**–**6** and **7b** are presented in Figs. 2–4.

CCDC reference numbers 162466–162470.

See http://www.rsc.org/suppdata/dt/b1/b103067c/ for crystallographic data in CIF or other electronic format.

Computational details

The geometries of all of the complexes were optimised using the B3PW91 hybrid density functional method and employing 6-31G* as a basis set (for ruthenium: Huzinaga's extra basis 433321/4331/421),[20] and the geometry optimisations were followed by the frequency calculations necessary to obtain the vibration spectra of all the complexes. The calculations were carried out with Gaussian 98 program.[21]

Results and discussion

The 4,4′-disubstituted-2,2′-bipyridine complexes of ruthenium were synthesised and analysed using spectroscopic methods combined with a routine elemental analysis. The electronic effects of the different substituents were analysed by means of spectroscopic and theoretical methods. The role of the

Table 1 Crystallographic data for complexes (4,4′-L_2-2,2′-bpy)Ru$(CO)_2Cl_2$ (**3**–**6**, **7b**)

	3	**4**	**5**	**6**	**7b**
Empirical formula	$C_{21}H_{26}Cl_4N_2O_2Ru$	$C_{21}H_{25}Cl_5N_2O_2Ru$	$C_{12}H_6Cl_2N_4O_6Ru$	$C_{12}H_{17}Cl_2N_2O_{11.5}P_2Ru$	$C_{14.5}H_{11}Cl_3N_2O_{4.5}Ru$
FW	581.31	615.75	474.18	607.19	492.67
Crystal system	Monoclinic	Orthorhombic	Orthorhombic	Monoclinic	Triclinic
Space group	$P2_1/n$	*Pmna*	*Fdd*2	$P2_1/c$	$P\bar{1}$
λ/Å	0.71073	0.71073	0.71073	0.71073	0.71073
a/Å	10.5585(1)	12.1131(1)	21.6703(9)	12.9936(3)	9.8788(4)
b/Å	11.4729(1)	13.9583(2)	38.6235(5)	26.5886(7)	9.9646(5)
c/Å	21.2337(2)	15.9437(2)	7.8367(2)	12.1315(3)	10.6567(5)
α/°					72.402(2)
β/°	98.7539(5)			99.9532(16)	74.689(3)
γ/°					69.284(2)
V/Å^3	2542.22(4)	2695.73(6)	6559.2(3)	4128.13(18)	920.65(7)
T/K	150(2)	120(2)	120(2)	120(2)	120(2)
Z	4	4	16	8	2
D_{calc}/g cm^{-3}	1.519	1.517	1.921	1.954	1.777
μ/mm^{-1}	1.056	1.097	1.320	1.236	1.311
No. reflections collected	10289	33328	24184	40510	7464
No. unique reflections	5300	2542	3176	7179	3783
R_{int}	0.0110	0.0373	0.0480	0.1061	0.0135
$R1$ ($I > 2\sigma$)	0.0380	0.0461	0.0242	0.0605	0.0257
$wR2$ ($I > 2\sigma$)	0.0954	0.1194	0.0458	0.1250	0.0612

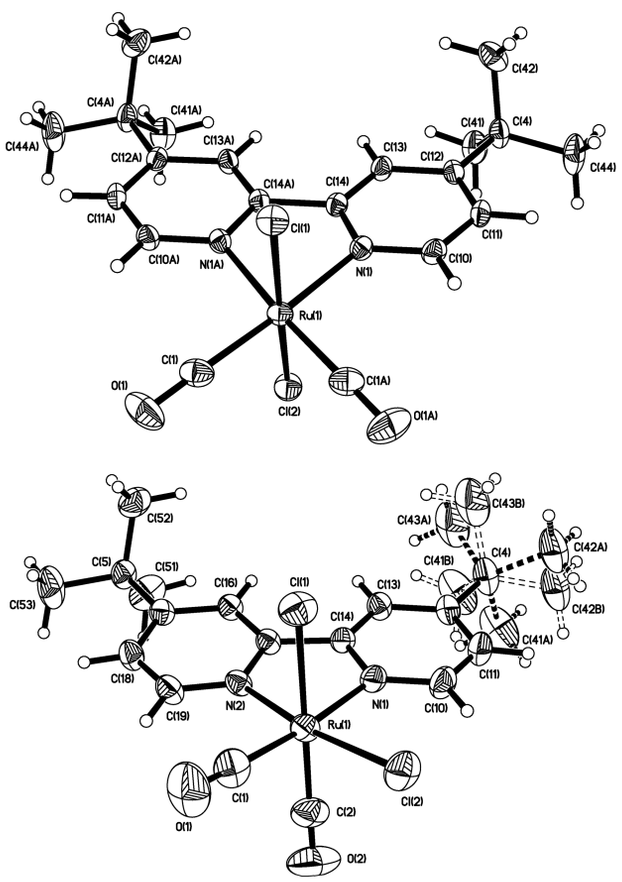

Fig. 2 X-Ray crystal structures of complexes **3** (top) and **4** (bottom); *trans*(Cl)- and *cis*(Cl),*cis*(CO)-(4,4′-di-*tert*-butyl-2,2′-bipyridine)Ru$(CO)_2Cl_2$.

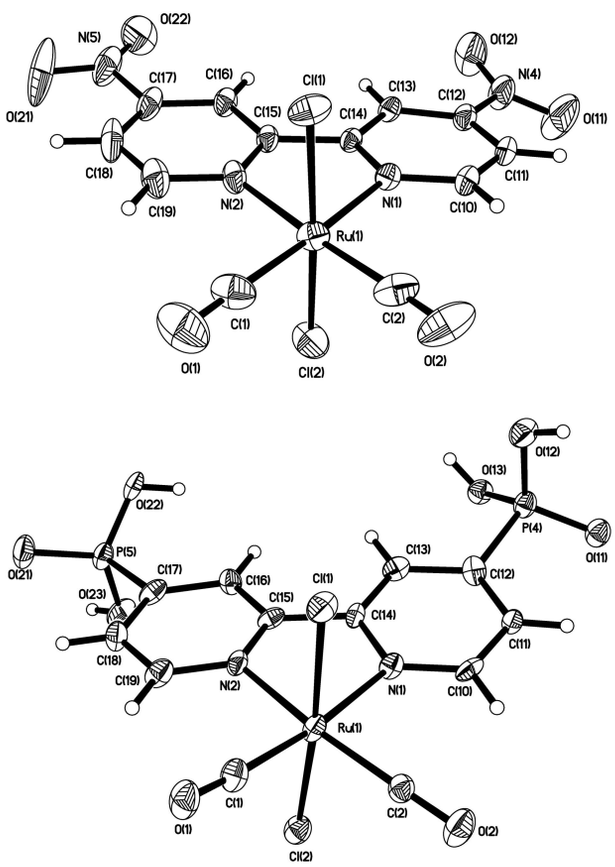

Fig. 3 X-Ray crystal structures of complexes **5** (top) and **6** (bottom); *trans*(Cl)-(4,4′-L_2-2,2′-bipyridine)Ru$(CO)_2Cl_2$.

electronic properties of the substituent was observed experimentally as a shift of visible light absorption band. Density functional calculations showed that the electronic effect of the substituent on the complex involved two main properties. The substituent variation effects on the HOMO–LUMO energies and, secondly, the positions of the ν_{CO} bands in the IR spectrum were calculated to be dependent on the substituents.

As electron donors, the alkyl substituents (Me and *t*-Bu) shifted the absorption maximum to lower wavelength, while the electron withdrawing groups acted in the reverse way. The trend observed in our study is in agreement with the literature, the energy of the charge transfer from a metal to a ligand has been reported to effect the absorption spectrum.[7b] The value of this transfer energy is dependent on the electronic nature of the ligand system. The energy differences between the HOMO and LUMO orbitals were calculated by the hybrid density functional method B3PW91 using the 6-31G* basis set and on the other hand, with Hartree–Fock single point calculation for the optimised structure. The density functional calculations successfully predicted the geometries of the ruthenium complexes. The computational and experimental bond lengths and angles of the coordination sphere of Ru are compared in Table 2. In *cis*(Cl),*cis*(CO)-complex **4** the coordination sphere around the

Table 2 Experimental and calculated bond lengths (Å) and angles (°) of complexes **3**–**6**

	3		**4**		**5**		**6**	
	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.[a]	Calc.
Ru–N1	2.107(3)	2.152	2.099(2)	2.146	2.113(2)	2.115	2.113(7), 2.130(7)	2.150
Ru–N2	2.107(3)	2.152	2.065(2)	2.100	2.106(3)	2.115	2.099(7), 2.137(7)	2.150
Ru–C1	1.878(4)	1.870	1.926(4)	1.880	1.877(4)	1.880	1.888(9), 1.893(9)	1.870
Ru–C2	1.878(4)	1.870	1.868(4)	1.870	1.890(4)	1.880	1.870(9), 1.864(1)	1.870
Ru–Cl1	2.398(1)	2.440	2.408(5)	2.430	2.377(8)	2.430	2.397(2), 2.394(2)	2.430
Ru–Cl2	2.385(2)	2.430	2.411(6)	2.420	2.379(8)	2.430	2.395(2), 2.388(2)	2.430
C1–O1	1.137(5)	1.140	1.091(4)	1.140	1.118(4)	1.140	1.137(1), 1.132(1)	1.140
C2–O2	1.137(5)	1.140	1.132(4)	1.150	1.122(4)	1.140	1.136(1), 1.148(1)	1.140
N1–Ru–N2	77.27(2)	76.18	77.65(9)	76.98	77.14(9)	76.56	77.10(3), 77.10(3)	76.45
C1–Ru–C2	88.00(3)	89.64	91.96(2)	93.30	84.96(2)	89.27	89.90(4), 87.70(4)	89.440
Cl1–Ru–Cl2	174.7(5)	172.38	91.03(3)	92.87	173.0(7)	172.34	174.1(4), 176.1(8)	172.46
Ru–C1–O1	178.4(4)	177.94	175.8(4)	178.52	179.0(4)	177.96	173.3(8), 175.9(8)	178.00
Ru–C2–O2	178.4(4)	177.94	179.2(4)	179.64	176.6(3)	177.97	174.5(8), 175.8(8)	178.00

[a] The asymmetric unit contains two molecules; **6** and **6b**.

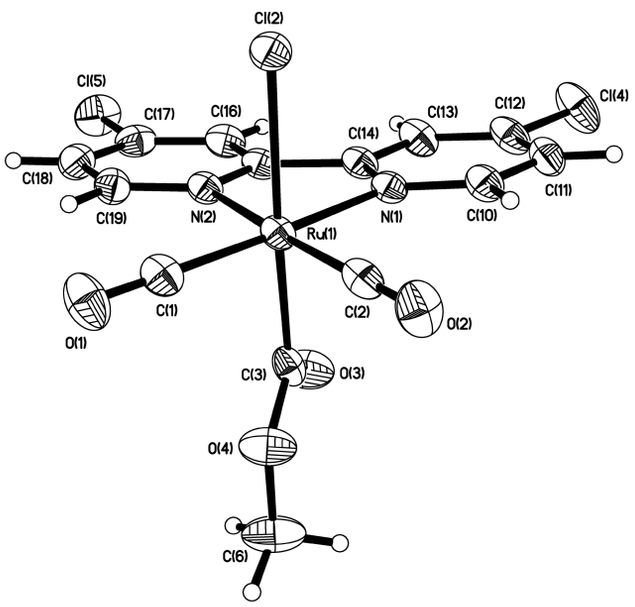

Fig. 4 X-Ray crystal structure of complex **7b**; (4,4′-dichloro-2,2′-bipyridine)$Ru(CO)_2Cl(C(O)OCH_3)$. Selected bond lengths (Å) and angles (°): Ru1–N1 2.106(2), Ru1–N2 2.114(7), Ru1–C1 1.879(3), Ru1–C2 1.891(3), Ru1–Cl2 2.481(8), C1–O1 1.131(3), C2–O2 1.138(3); N1–Ru1–N2 77.38(8), C1–Ru1–C2 88.01(1), Ru1–C1–O1 178.9(2), Ru1–C2–O2 179.5(3).

ruthenium centre is less symmetrical. Due to this ligand arrangement there is some variation in the Ru–C and Ru–N bond lengths. The axial Ru1–C2 length is slightly shorter than the corresponding equatorial Ru1–C1. Ru1–N2 *trans* to Cl(2) is also slightly shorter than the Ru1–N1 bond *trans* to the CO ligand. As can be seen, the computational method tends to overestimate the Ru–N bond lengths, which is typical for the DFT procedure used.[22] Similarly, the Ru–Cl bonds are slightly overestimated. Otherwise the agreement with the experimental results is good. It should be remembered that the calculations were carried out without taking into account the intermolecular interactions.

The HOMO–LUMO energy differences and the correlation with the absorption maximum values are summarised in Table 3 and Fig. 5, from which the electronic effect of the substituent can be clearly seen: the lower the HOMO–LUMO difference, the higher wavelength of the absorption maximum. Substituents that are coordinated directly to the metal centre have recently been reported to affect the position of the absorption band in the UV-Vis spectrum.[23]

Table 3 HOMO–LUMO energy differences and absorption maxima for complexes *trans*(Cl)-(4,4′-L_2-2,2′-bpy)$Ru(CO)_2Cl_2$

L	Δ*E*/eV (HF)[a]	Δ*E*/eV (B3PW91)	λ_{max}/nm
NO_2	9.40	2.30	401
H_2PO_3	9.98	2.87	358
Cl	10.17	2.97	356
Br	10.16	2.97	356
H	10.36	3.13	342
Me	10.36	3.18	334
t-Bu	10.47	3.30	334

[a] Hartree–Fock method.

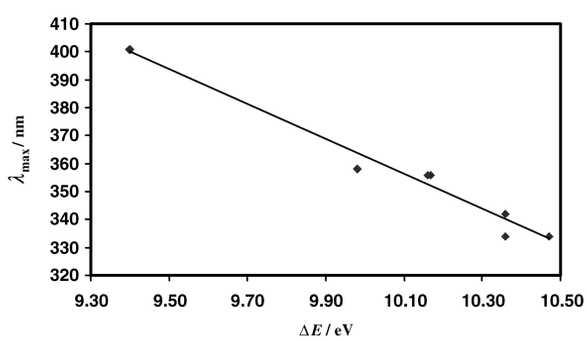

Fig. 5 The correlation between the HOMO–LUMO energy difference and metal-to-ligand charge-transfer absorption maximum.

All of our eight complexes contained two carbonyls, which were coordinated to the ruthenium centre. The calculated and experimental IR spectra indicated a substituent-sensitive shift for the CO-stretching band. The calculated values were corrected using the correlation coefficients (0.9509 for the asymmetric vibration and 0.9570 for the symmetric vibration) purely to match the computational values to the experimental spectra. The data for the CO-stretching is summarised in Table 4. The electronic properties of the substituents affect the ruthenium charge, resulting in a slight variation in the CO-vibration wavenumbers compared with the unsubstituted complex (Fig. 6). Both the experimental and the theoretical values reveal similarities in the spectra of the two different isomers. The coordination site (axial or the equatorial) of the carbonyl does not have a strong impact on the position of the CO-vibration band. Thus, reliable isomer identification is difficult when using only IR spectroscopy, while in most cases NMR-spectral data is required to the determine the isomeric structure.

Table 4 Theoretical and experimental IR data for the carbonyl stretching of the (4,4′-L_2-2,2′-bpy)$Ru(CO)_2Cl_2$ complexes

		Theoretical/cm^{-1}		Corrected/cm^{-1}		Experimental[a]/cm^{-1}		Effect of substituent L[c]/cm^{-1}	
Isomer	L	ν_{as} (CO)	ν_s (CO)	ν_{as} (CO)	ν_s (CO)	ν_{as} (CO)	ν_s (CO)	ν_{as} (CO)	ν_s (CO)
trans(Cl)	*t*-Bu	2106	2157	2003	2064	2000	2066	−2	−2
trans(Cl)	Me	2107	2157	2004	2064	2003	2067	−1	−2
trans(Cl)	H	2109	2159	2005	2066	2003[e]	2066[e]	—	—
trans(Cl)	Cl	2112	2162	2008	2069	2007	2068	+3	+3
trans(Cl)	Br	2112	2162	2008	2069	2008	2067	+3	+3
trans(Cl)	H_2PO_3	2110	2163	2006	2070	2011[b]	2073[b]	+7	+6
trans(Cl)	NO_2	2120	2167	2016	2074	2018	2074	+11	+8
cis(Cl)	*t*-Bu	2103	2157	2000	2064	2000	2065	−4	−4
cis(Cl)	Me	2104	2159	2001	2066	2003[d]	2066[d]	−3	−2
cis(Cl)	H	2107	2161	2004	2068	2003[e]	2067[e]	—	—
cis(Cl)	Cl	2110	2163	2006	2070			+2	+2
cis(Cl)	Br	2110	2163	2006	2070			+2	+2
cis(Cl)	H_2PO_3	2112	2161	2008	2068			+8	+6
cis(Cl)	NO_2	2119	2169	2015	2076			+11	+8

[a] Experimental values measured in CH_2Cl_2. [b] Measured in MeOH because of the poor solubility in CH_2Cl_2. [c] Corrected values compared to unsubstituted complex **1**. [d] Ref. 24. [e] Ref. 25.

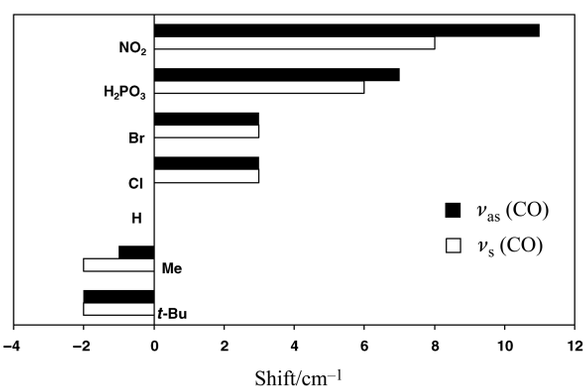

Fig. 6 The effect of substituent L on the CO-stretching band for *trans*(Cl)-(4,4′-L_2-2,2′-bpy)$Ru(CO)_2Cl_2$ complexes.

Conclusions

Both the theoretical and the experimental study revealed clearly the electronic effect of the ligand substituents in the ruthenium monobipyridine complexes, and the electron withdrawing properties of the substituents clearly affected the absorption and vibration spectra. The electron withdrawing substituents Cl, Br, NO_2 and H_2PO_3 shifted the absorption band to a higher wavelength, while the electron donating alkyl substituents acted in the opposite way. In the IR spectrum the carbonyl-stretching band was also slightly shifted in comparison to the spectrum of the unsubstituted complex. Again, the electron withdrawing properties of the substituents determined the direction and extent of the CO band shifting: the electron acceptors increased and the electron donors decreased wavenumbers of the ν_{CO} bands. Finally, our results show that the prediction of the position of the carbonyl band in the IR spectrum can be made on the basis of the electronic character of the ligand system. On the other hand, modification of the ligand system can be used to produce complexes with the absorption properties required.

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