Molecular quadratic non-linear optical properties of dipolar *trans*-tetraammineruthenium(II) complexes with pyridinium and thiocyanate ligands

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Seven new complex salts *trans*-[Ru^{II}(NCS)(NH$_3$)$_4$(L^A)][PF$_6$]$_2$ [L^A = *N*-methyl-4,4′-bipyridinium (MeQ$^+$) **1**, *N*-methyl-2,7-diazapyrenium (Medap$^+$) **2**, *N*-methyl-4-[*trans*-2-(4-pyridyl)ethenyl]pyridinium (Mebpe$^+$) **3**, *N*-phenyl-4,4′-bipyridinium (PhQ$^+$) **4**, *N*-phenyl-4-[*trans*-2-(4-pyridyl)ethenyl]pyridinium (Phbpe$^+$) **5**, *N*-(4-acetylphenyl)-4,4′-bipyridinium (4-AcPhQ$^+$) **6**, or *N*-(2-pyrimidyl)-4,4′-bipyridinium (2-PymQ$^+$) **7**] have been prepared. The electronic absorption spectra of **1**–**7** display intense, visible metal-to-ligand charge-transfer (MLCT) bands, the energies (E_{max}) of which decrease in the order **2** > **1** > **3** > **4** > **6** > **5** > **7**, as the electron-accepting ability of L^A increases. The E_{max} values generally correlate with cyclic voltammetric and ^{1}H NMR data. Comparisons of the MLCT absorption and electrochemical data for **1**–**7** show that a *trans*-{Ru^{II}(NCS)(NH$_3$)$_4$}$^+$ centre is a stronger electron donor than analogous groups containing only neutral ligands. Molecular first hyperpolarizabilities β have been measured by using the hyper-Rayleigh scattering technique with acetonitrile solutions and a 1064 nm laser, and static first hyperpolarizabilities β_0[H] were obtained by application of the two-state model. Stark (electroabsorption) spectroscopic studies in butyronitrile glasses at 77 K have afforded dipole moment changes $\Delta\mu_{12}$ for the MLCT transitions which have been used to calculate β_0[S] values according to the two-state equation $\beta_0 = 3\Delta\mu_{12}(\mu_{12})^2/(E_{max})^2$ (μ_{12} = transition dipole moment). Both the β_0[H] and β_0[S] data confirm that the increased electron donor ability of a *trans*-{Ru^{II}(NCS)(NH$_3$)$_4$}$^+$ centre affords enhanced β_0 values, when compared with related complexes containing the neutral *trans* ligands NH$_3$, 4-(dimethylamino)pyridine, *N*-methylimidazole (mim) or pyridine. However, the magnitude of the observed β_0 increase with respect to the analogous mim complexes varies over a range of *ca.* 25–120%, depending upon L^A.

Introduction

The potential benefits of optoelectronic or even all-optical (photonic) data processing in terms of speed and scale of operation have inspired a vast research effort involving materials with nonlinear optical (NLO) properties. Molecular organic materials are especially promising because they can exhibit very large NLO responses which can be tuned *via* synthetic chemistry, and they may also be readily processed for device applications.[1] Organotransition metal complexes offer many interesting possibilities for combining NLO effects with other molecular electronic properties (*e.g.* redox or magnetic behaviour) to afford novel multifunctional materials.[2] Recent research involving such compounds has focused on the establishment of molecular structure–activity correlations, which are currently considerably better developed for purely organic NLO chromophores.

Quadratic (second-order) NLO properties derive at the molecular level from first hyperpolarizability coefficients β. Molecules with large β values typically comprise a strong electron donor (D) group connected to an electron acceptor (A) *via* a conjugated π-bridge. Their linear optical properties are therefore dominated by intense, low energy D(π)⟶(π*) charge-transfer (CT) transitions, and resonance can have pronounced enhancing effects on experimentally measured β values. Static first hyperpolarizabilities β_0, which can be estimated by application of a widely used two-state model for dipolar chromophores,[3] are a measure of the intrinsic NLO response under non-resonant (*i.e.* working) conditions. We have found that ruthenium pyridyl ammines with pyridinium A groups can have very large β_0 values which are associated with intense, low energy metal-to-ligand CT (MLCT) excitations.[4] The MLCT absorption and NLO properties of these complexes are highly tunable by changes in ligand structure and can also be reversibly switched *via* the Ru$^{III/II}$ redox couple.[5] Furthermore, quantitative comparisons show that a pyridyl-coordinated {Ru^{II}(NH$_3$)$_5$}$^{2+}$ centre is a more effective π-electron donor than the widely used 4-(dimethylamino)phenyl group, because the higher HOMO energy of the Ru^{II} centre more than offsets the stronger π-orbital overlap in analogous purely organic chromophores.[6]

Our previous studies with complexes *trans*-[Ru^{II}(NH$_3$)$_4$L-(L^A)]$^{3+}$ (L = electron-rich ligand, L^A = pyridyl pyridinium ligand) have largely focused on changes in the structure of L^A, with the primary aim of increasing its electron accepting ability.[4] However, the electron-donating strength of the Ru^{II} centre can also be modified by changing L. To date, we have used only neutral ligands, and in order to further increase the electron donor strength, anionic ligands are attractive candidates. The Lever electrochemical parameters show that common anions are considerably better electron donors towards Ru^{II} when compared with ligands such as NH$_3$.[7] Herein we report the syntheses of a new series of thiocyanate-containing complex salts *trans*-[Ru^{II}(NCS)(NH$_3$)$_4$(L^A)][PF$_6$]$_2$ and their study by using

various techniques including hyper-Rayleigh scattering (HRS) measurements[8] and Stark (electroabsorption) spectroscopy.[9]

Experimental

Materials and procedures

The salts *trans*-[Ru^{III}(SO$_4$)(NH$_3$)$_4$(L^A)]Cl$_2$ [L^A = *N*-methyl-4,4′-bipyridinium (MeQ$^+$),[4a] *N*-methyl-2,7-diazapyrenium (Medap$^+$),[4d] *N*-methyl-4-[*trans*-2-(4-pyridyl)ethenyl]pyridinium (Mebpe$^+$),[4d] *N*-phenyl-4,4′-bipyridinium (PhQ$^+$)[4c] or *N*-(4-acetylphenyl)-4,4′-bipyridinium (4-AcPhQ$^+$)][4c] were synthesized from *trans*-[Ru^{II}Cl(NH$_3$)$_4$(SO$_2$)]Cl[10] according to previously published methods. The closely similar compounds *trans*-[Ru^{III}(SO$_4$)(NH$_3$)$_4$(L^A)]Cl$_2$ [L^A = *N*-phenyl-4-[*trans*-2-(4-pyridyl)ethenyl]pyridinium (Phbpe$^+$) or *N*-(2-pyrimidyl)-4,4′-bipyridinium (2-PymQ$^+$)] were prepared in an identical fashion, by using the pro-ligand salts [Phbpe$^+$]Cl and [2-PymQ$^+$]Cl.[4d] These sulfate complex salts are merely synthetic intermediates and are used without purification or characterization; the yields of **1**–**7** are hence quoted with respect to their universal precursor *trans*-[Ru^{II}Cl(NH$_3$)$_4$(SO$_2$)]Cl. All reactions were performed under an argon atmosphere and in argon-purged solvents, and all reactions and chromatographic purifications were performed in the dark. Products were dried overnight in a vacuum desiccator (CaCl$_2$) prior to characterization.

General physical measurements

Proton NMR spectra were recorded on a Varian XL-300 spectrometer and all shifts are referenced to SiMe$_4$. The fine splitting of pyridyl or phenyl ring AA′BB′ patterns is ignored and the signals are reported as simple doublets, with *J* values referring to the two most intense peaks. Elemental analyses were performed by the Microanalytical Laboratory, University of Manchester and UV/VIS spectra were obtained by using a Hewlett Packard 8452A diode array spectrophotometer. IR spectra were recorded as KBr disks with a Perkin Elmer RX-1 FTIR spectrometer and mass spectra were measured by using +electrospray on a Micromass Platform spectrometer with acetone as the solvent (cone voltage 30 V). The numbers reported correspond to the most intense peaks of the ion envelopes.

Cyclic voltammetric measurements were carried out by using an EG&G PAR model 283 potentiostat/galvanostat. A single-compartment cell was used with a silver/silver chloride reference electrode, a platinum-disc working electrode and a platinum-wire auxiliary electrode. Acetonitrile was freshly distilled (from CaH$_2$) and tetra-*n*-butyl ammonium hexafluorophosphate, twice recrystallized from ethanol and dried *in vacuo*, was used as the supporting electrolyte. Solutions containing *ca.* 10^{-3} mol dm^{-3} analyte (0.1 mol dm^{-3} electrolyte) were deaerated by purging with N$_2$. All $E_{1/2}$ values were calculated from (E_{pa} + E_{pc})/2 at a scan rate of 200 mV s^{-1}.

Syntheses

***trans*-[Ru^{II}(NCS)(NH$_3$)$_4$(MeQ$^+$)][PF$_6$]$_2$ 1.** A solution of *trans*-[Ru^{III}(SO$_4$)(NH$_3$)$_4$(MeQ$^+$)]Cl$_2$ (unweighed, derived from *trans*-[Ru^{II}Cl(NH$_3$)$_4$(SO$_2$)]Cl, 100 mg, 0.329 mmol) in water (10 cm^3) was reduced over zinc amalgam (4 lumps) with argon agitation for 15 min. This was filtered under argon into a flask containing KNCS (160 mg, 1.65 mmol), further water (*ca.* 30 cm^3) was added to solubilise the intially formed dark precipitate, and the solution was stirred at room temperature in the dark under argon for 4 h. Excess aqueous NH$_4$PF$_6$ (0.2 M) was added to precipitate the dark blue crude product which was filtered off, washed with a small amount of cold water, then ethanol and dried. The solid was dissolved in acetone and purified by column chromatography on silica gel (400 g). The column was packed with a chloroform slurry and elution with

NH$_4$PF$_6$ in methanol–acetone–acetonitrile (1 : 3 : 1) (0.1 M) gave a major blue band from which the most intense section was collected. This solution was diluted five-fold with diethyl ether. The dark blue precipitate was filtered off, washed with a small amount of cold water, ethanol, then diethyl ether and dried: yield 49 mg (22%). δ_H (CD$_3$COCD$_3$) 9.15 (2 H, d, *J* 6.7, C$_5$H$_4$N), 9.09 (2 H, d, *J* 6.9, C$_5$H$_4$N), 8.70 (2 H, d, *J* 6.9, C$_5$H$_4$N), 7.90 (2 H, d, *J* 6.7, C$_5$H$_4$N), 4.44 (3 H, s, Me), 2.63 (12 H, s, 4NH$_3$). ν(C≡N) 2109s cm^{-1}, ν(C–S) expected at *ca.* 800 cm^{-1}, but not observed due to overlap by an intense and broad ν(P–F) band at 840 cm^{-1} (Found: C, 20.90; H, 3.18; N, 13.56. Calc. for C$_{12}$H$_{23}$F$_{12}$N$_7$P$_2$RuS: C, 20.94; H, 3.37; N 14.24%). *m/z*: 543 ([M − PF$_6^-$]$^+$).

***trans*-[Ru^{II}(NCS)(NH$_3$)$_4$(Medap$^+$)][PF$_6$]$_2$ 2.** This was prepared and purified in similar manner to **1** by using *trans*-[Ru^{III}-(SO$_4$)(NH$_3$)$_4$(Medap$^+$)]Cl$_2$ (unweighed, derived from *trans*-[Ru^{II}-Cl(NH$_3$)$_4$(SO$_2$)]Cl, 200 mg, 0.658 mmol) in water (60 cm^3) and KNCS (320 mg, 3.29 mmol) with a reaction time of 5 h. A dark blue solid was obtained: yield 68 mg (14%). δ_H (CD$_3$COCD$_3$) 10.01 (2 H, s, C$_{14}$H$_8$N$_2$), 9.83 (2 H, s, C$_{14}$H$_8$N$_2$), 8.56 (2 H, d, *J* 9.2, C$_{14}$H$_8$N$_2$), 8.47 (2 H, d, *J* 9.2, C$_{14}$H$_8$N$_2$), 4.89 (3 H, s, Me), 2.70 (12 H, s, 4NH$_3$). ν(C≡N) 2103s cm^{-1} (Found: C, 26.00; H, 2.98; N, 12.93. Calc. for C$_{16}$H$_{23}$F$_{12}$N$_7$P$_2$RuS: C, 26.09; H, 3.15; N, 13.31%). *m/z*: 590 ([M − PF$_6^-$]$^+$).

***trans*-[Ru^{II}(NCS)(NH$_3$)$_4$(Mebpe$^+$)][PF$_6$]$_2$ 3.** This was prepared and purified in similar manner to **1** by using *trans*-[Ru^{III}-(SO$_4$)(NH$_3$)$_4$(Mebpe$^+$)]Cl$_2$ (unweighed, derived from *trans*-[Ru^{II}-Cl(NH$_3$)$_4$(SO$_2$)]Cl, 150 mg, 0.493 mmol) and KNCS (170 mg, 1.75 mmol). A dark blue solid was obtained: yield 30 mg (9%). δ_H (CD$_3$COCD$_3$) 8.97 (2 H, d, *J* 6.8, C$_5$H$_4$N), 8.91 (2 H, d, *J* 5.8, C$_5$H$_4$N), 8.34 (2 H, d, *J* 6.8, C$_5$H$_4$N), 8.05 (1 H, d, *J* 16.4, CH), 7.91 (1 H, d, *J* 16.4, CH), 7.54 (2 H, d, *J* 5.8, C$_5$H$_4$N), 4.50 (3 H, s, Me), 2.63 (12 H, s, 4NH$_3$). ν(C≡N) 2102s cm^{-1} (Found: C, 23.69; H, 3.33; N, 13.94. Calc. for C$_{14}$H$_{25}$F$_{12}$N$_7$P$_2$RuS: C, 23.54; H, 3.53; N, 13.72%). *m/z*: 569 ([M − PF$_6^-$]$^+$).

***trans*-[Ru^{II}(NCS)(NH$_3$)$_4$(PhQ$^+$)][PF$_6$]$_2$ 4.** This was prepared and purified in similar manner to **1** by using *trans*-[Ru^{III}-(SO$_4$)(NH$_3$)$_4$(PhQ$^+$)]Cl$_2$ (unweighed, derived from *trans*-[Ru^{II}-Cl(NH$_3$)$_4$(SO$_2$)]Cl, 100 mg, 0.329 mmol) and KNCS (113 mg, 1.16 mmol) with a reaction time of 3 h. A dark blue solid was obtained: yield 51 mg (21%). δ_H (CD$_3$COCD$_3$) 9.37 (2 H, d, *J* 7.1, C$_5$H$_4$N), 9.23 (2 H, d, *J* 7.0, C$_5$H$_4$N), 8.88 (2 H, d, *J* 7.0, C$_5$H$_4$N), 8.01–7.96 (4 H, m, C$_5$H$_4$N and Ph), 7.84–7.79 (3 H, m, Ph), 2.66 (12 H, s, 4NH$_3$). ν(C≡N) 2102s cm^{-1} (Found: C, 27.32; H, 3.33; N, 12.43. Calc. for C$_{17}$H$_{25}$F$_{12}$N$_7$P$_2$RuS: C, 27.21; H, 3.36; N, 13.06%). *m/z*: 606 ([M − PF$_6^-$]$^+$).

***trans*-[Ru^{II}(NCS)(NH$_3$)$_4$(Phbpe$^+$)][PF$_6$]$_2$ 5.** This was prepared and purified in similar manner to **1** by using *trans*-[Ru^{III}-(SO$_4$)(NH$_3$)$_4$(Phbpe$^+$)]Cl$_2$ (unweighed, derived from *trans*-[Ru^{II}-Cl(NH$_3$)$_4$(SO$_2$)]Cl, 136 mg, 0.447 mmol) in water (30 cm^3) and KNCS (160 mg, 1.65 mmol). A dark blue solid was obtained: yield 51 mg (15%). δ_H (CD$_3$COCD$_3$) 9.25 (2 H, d, *J* 7.0, C$_5$H$_4$N), 8.97 (2 H, d, *J* 6.7, C$_5$H$_4$N), 8.51 (2 H, d, *J* 7.0, C$_5$H$_4$N), 8.18 (1 H, d, *J* 16.3, CH), 8.04 (1 H, d, *J* 16.3, CH), 7.98–7.94 (2 H, m, Ph), 7.81–7.97 (3 H, m, Ph), 7.57 (2 H, d, *J* 6.7, C$_5$H$_4$N), 2.57 (12 H, s, 4NH$_3$). ν(C≡N) 2099s cm^{-1} (Found: C, 29.77; H, 3.32; N, 12.44. Calc. for C$_{19}$H$_{27}$F$_{12}$N$_7$P$_2$RuS: C, 29.39; H, 3.50; N, 12.63%). *m/z*: 631 ([M − PF$_6^-$]$^+$).

***trans*-[Ru^{II}(NCS)(NH$_3$)$_4$(4-AcPhQ$^+$)][PF$_6$]$_2$ 6.** This was prepared and purified in similar manner to **4** by using *trans*-[Ru^{III}-(SO$_4$)(NH$_3$)$_4$(4-AcPhQ$^+$)]Cl$_2$ (unweighed, derived from *trans*-[Ru^{II}Cl(NH$_3$)$_4$(SO$_2$)]Cl, 100 mg, 0.329 mmol) and KNCS (160 mg, 1.65 mmol). A dark blue solid was obtained: yield

48 mg (18%). δ_H (CD$_3$COCD$_3$) 9.50 (2 H, d, J 7.2, C$_5$H$_4$N), 9.12 (2 H, d, J 7.1, C$_5$H$_4$N), 8.95 (2 H, d, J 7.2, C$_5$H$_4$N), 8.40 (2 H, d, J 8.7, C$_6$H$_4$), 8.20–8.16 (4 H, m, C$_5$H$_4$N and C$_6$H$_4$), 2.78 (3 H, s, C(O)Me) 2.64 (12 H, s, 4NH$_3$). ν(C≡N) 2104s cm^{-1}, ν(C=O) 1686s cm^{-1} (Found: C, 28.41; H, 3.29; N, 11.99. Calc. for C$_{19}$H$_{27}$F$_{12}$N$_7$OP$_2$RuS: C, 28.80; H, 3.43; N, 12.37%). m/z: 648 ([M − PF$_6^-$]$^+$).

***trans*-[Ru^{II}(NCS)(NH$_3$)$_4$(2-PymQ$^+$)][PF$_6$]$_2$ 7.** This was prepared and purified in similar manner to **4** by using *trans*-[Ru^{III}-(SO$_4$)(NH$_3$)$_4$(2-PymQ$^+$)]Cl$_2$ (unweighed, derived from *trans*-[Ru^{III}Cl(NH$_3$)$_4$(SO$_2$)]Cl, 100 mg, 0.329 mmol) and KNCS (164 mg, 1.69 mmol). A dark blue solid was obtained: yield 54 mg (22%). δ_H (CD$_3$COCD$_3$) 10.17 (2 H, d, J 7.4, C$_5$H$_4$N), 9.25–9.22 (4 H, m, C$_5$H$_4$N and C$_4$H$_3$N$_2$), 8.92 (2 H, d, J 7.4, C$_5$H$_4$N), 8.04–7.99 (3 H, m, C$_5$H$_4$N and C$_4$H$_3$N$_2$), 2.69 (12 H, s, 4NH$_3$). ν(C≡N) 2103s cm^{-1} (Found: C, 24.32; H, 3.48; N, 16.22. Calc. for C$_{15}$H$_{23}$F$_{12}$N$_9$P$_2$RuS: C, 23.94; H, 3.08; N, 16.75%). m/z: 607 ([M − PF$_6^-$]$^+$).

Hyper-Rayleigh scattering

Details of the hyper-Rayleigh scattering (HRS) experiment have been discussed elsewhere,[3c,8b–d] and the experimental procedure used was as previously described.[11] Values of β were determined by using the electric-field-induced second harmonic generation β_{1064} for p-nitroaniline (29.2 × 10^{-30} esu in acetonitrile)[12] as an external reference. All measurements were performed by using the 1064 nm fundamental of an injection-seeded, Q-switched Nd-YAG laser (Quanta-Ray GCR-5, 8 ns pulses, 7 mJ, 10 Hz). Dilute acetonitrile solutions (10^{-5}–10^{-6} mol dm^{-3}) were used to ensure a linear dependence of $I_{2\omega}/I_\omega^2$ on solute concentration, precluding the need for Lambert–Beer correction factors. Samples were filtered (Millipore, 0.45 μm), and none showed any fluorescence. One-dimensional hyperpolarizability is assumed, *i.e.* $\beta_{1064} = \beta_{333}$, and a relative error of ±15% is estimated.

Stark spectroscopy

The electroabsorption apparatus, experimental methods and data analysis procedure were exactly as previously reported,[4e,13] with the only modification being that a Xe arc lamp was used as the light source in the place of a tungsten filament bulb. Butyronitrile was used as the glassing medium, for which the local field correction f_{int} is estimated as 1.33.[4e,13] The Stark spectrum for each compound was measured a minimum of three times using different field strengths, and the signal was always found to be quadratic in the applied field. A two-state analysis of the MLCT transitions gives

$$\Delta\mu_{ab}^2 = \Delta\mu_{12}^2 + 4\mu_{12}^2 \tag{1}$$

where $\Delta\mu_{ab}$ is the dipole moment difference between the diabatic states, $\Delta\mu_{12}$ is the observed (adiabatic) dipole moment difference, and μ_{12} is the transition dipole moment. The latter can be determined from the oscillator strength f_{os} of the transition by

$$|\mu_{12}| = \left[f_{os} / \left(1.08 \times 10^{-5} E_{max}\right) \right]^{1/2} \tag{2}$$

where E_{max} is the energy of the MLCT maximum (in wavenumbers). The degree of delocalization c_b^2 and electronic coupling matrix element H_{ab} for the diabatic states are given by

$$c_b^2 = \frac{1}{2}\left[1 - \left(\frac{\Delta\mu_{12}^2}{\Delta\mu_{12}^2 + 4\mu_{12}^2} \right)^{1/2} \right] \tag{3}$$

$$|H_{ab}| = \left| \frac{E_{max}\left(\mu_{12}\right)}{\Delta\mu_{ab}} \right| \tag{4}$$

If the hyperpolarizability tensor β_0 has only nonzero elements along the CT direction, then this quantity is given by

$$\beta_0 = \frac{3\Delta\mu_{12}\left(\mu_{12}\right)^2}{\left(E_{max}\right)^2} \tag{5}$$

A relative error of ±20% is estimated for β_0 values derived from eqn. (5).

Results and discussion

Molecular design and synthesis

Although many anionic ligands are capable of coordinating to a Ru^{II} centre, several factors had to be considered when choosing a suitable anion for the purposes of this study. Clearly, more strongly electron-donating anions (as indicated by their Lever parameters)[7] will make the Ru^{II} centre more electron-rich and therefore a better electron donor. However, if the Ru^{II} centre becomes too electron-rich, then it may be readily oxidised in air to give a more stable Ru^{III} species, which would no longer act as an electron donor. Other important considerations are the reaction conditions. The precursor *trans*-[Ru^{II}Cl(NH$_3$)$_4$(SO$_2$)]Cl[10] is normally used to prepare derivatives with neutral (usually N-donor) ligands, and these reactions are typically carried out in aqueous solutions. Hence, hydration can be expected to influence the efficiency of coordination of anionic ligands. For example, conversion of *trans*-[Ru^{II}Cl(NH$_3$)$_4$(SO$_2$)]Cl into derivatives such as *trans*-[Ru^{II}(NH$_3$)$_4$(SO$_2$)(L^A)]Cl$_3$ (L^A = PhQ$^+$, *etc.*) occurs efficiently in water at *ca.* 45 °C using the ligand salts [L^A]Cl.[4c] Clearly, chloride does not compete effectively with a pyridyl ligand under such conditions. Another important factor is that the reaction temperature for both the initial chloride substitution and the subsequent replacement of water in complexes *trans*-[Ru^{II}(NH$_3$)$_4$(H$_2$O)(L^A)]$^{3+}$ must necessarily be kept below *ca.* 60 °C in order to avoid undesirable substitutions of the ammine ligands.

The new salts *trans*-[Ru^{II}(NCS)(NH$_3$)$_4$(L^A)][PF$_6$]$_2$ (**1**–**7**) were prepared from *trans*-[Ru^{II}(NH$_3$)$_4$(SO$_2$)(L^A)]$^{3+}$ by using modifications of established procedures, but the isolated yields are somewhat variable and also considerably lower than those obtained when using neutral L ligands.[4a,c,d] Precipitation of the reactive intermediate aquo complexes *trans*-[Ru^{II}(NH$_3$)$_4$-(H$_2$O)(L^A)]$^{3+}$ (generated from Zn(Hg) reduction of the complexes *trans*-[Ru^{III}(SO$_4$)(NH$_3$)$_4$(L^A)]$^+$ in aqueous solution) as their NCS$^-$ salts can hinder the successful replacement of H$_2$O by NCS$^-$. Similar reactions with a number of other anions including cyanate and azide failed to afford the desired products in any significant quantities (despite gentle warming), presumably due to undesirably effective anion hydration. It is possible that moving to non-aqueous media will allow the preparation of such complexes, but this will require considerable changes to be made to the synthetic approach and is beyond the scope of present studies. By analogy with existing Ru^{II} thiocyanate complexes,[14] it is assumed that the NCS$^-$ ligands in **1**–**7** are N-coordinated.

Electronic spectroscopy studies

Electronic absorption spectra for the new complex salts **1**–**7** were recorded in acetonitrile and the results are presented in Table 1. As expected, all of the complexes show intense d$_\pi$(Ru^{II})→π*(L^A) MLCT bands with λ_{max} values in the region 620–740 nm. The Medap$^+$ complex in **2** also shows five intense UV absorptions due to intraligand π→π* excitations, whilst

Table 1 Electrochemical and UV/VIS data for complex salts *trans*-[Ru^{II}(NCS)(NH$_3$)$_4$(L^A)][PF$_6$]$_2$ in acetonitrile

		$E_{1/2}$/V *vs.* Ag–AgCl (ΔE_p/mV) [a]			
Salt	L^A	Ru$^{III/II}$	Ligand waves	λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) [b]	Assignment
1	MeQ$^+$	0.40 (80)	−0.84 (70)	628 (20 000)	d$_\pi$⟶π*(MeQ$^+$)
			−1.46 (70)	266 (17 500)	π⟶π*
2	Medap$^+$	0.41 (105)	−0.97 [c]	622 (18 000)	d$_\pi$⟶π*(Medap$^+$)
				400 (11 300)	π⟶π*
				380 (8800)	π⟶π*
				336 (24 600)	π⟶π*
				324 (22 000)	π⟶π*
				244 (31 700)	π⟶π*
3	Mebpe$^+$	0.36 (90)	−0.80 [c]	638 (19 200)	d$_\pi$⟶π*(Mebpe$^+$)
				312 (25 900)	π⟶π*
4	PhQ$^+$	0.42 (85)	−0.66 (70)	672 (21 300)	d$_\pi$⟶π*(PhQ$^+$)
			−1.27 (80)	282 (18 400)	π⟶π*
5	Phbpe$^+$	0.35 (75)	−0.67 [c]	676 (17 400)	d$_\pi$⟶π*(Phbpe$^+$)
				332 (24 300)	π⟶π*
6	4-AcPhQ$^+$	0.41 (90)	−0.59 (80)	692 (18 400)	d$_\pi$⟶π*(4-AcPhQ$^+$)
			−1.14 (85)	284 (19 000)	π⟶π*
7	2-PymQ$^+$	0.42 (75)	−0.46 [c]	738 (21 800)	d$_\pi$⟶π*(2-PymQ$^+$)
				286 (18 900)	π⟶π*

[a] Measured in solutions *ca.* 10^{-3} mol dm^{-3} in analyte and 0.1 mol dm^{-3} in NBu$^n_4$PF$_6$ at a platinum-disc working electrode with a scan rate of 200 mV s^{-1}. Ferrocene internal reference $E_{1/2}$ = 0.46 V, ΔE_p = 70 mV. [b] Solutions *ca.* 5×10^{-5} mol dm^{-3}. [c] E_{pc} for an irreversible reduction process.
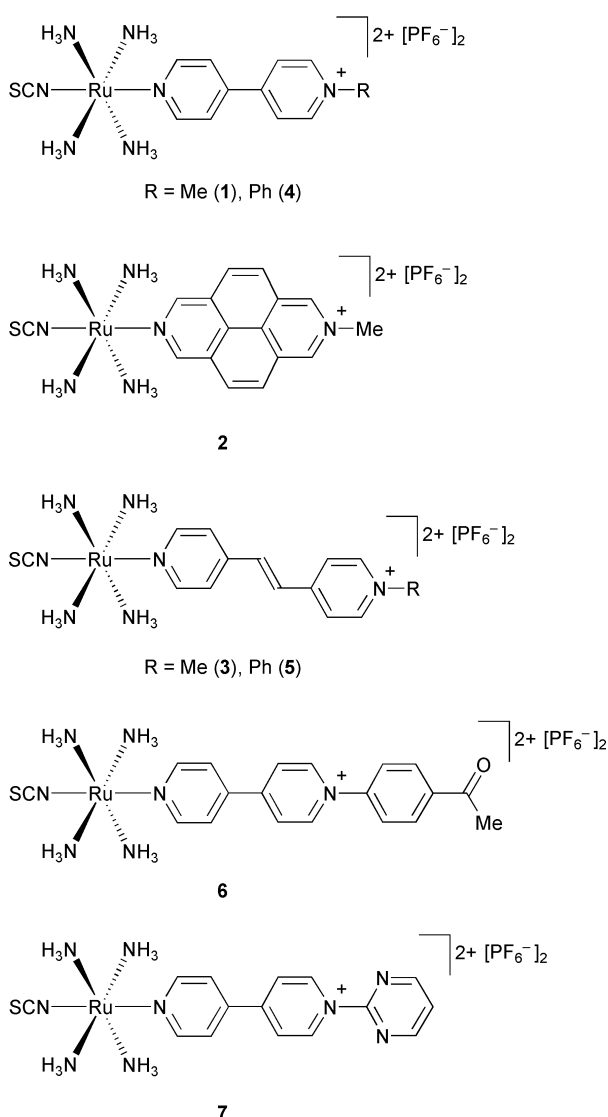
each of the other complexes shows only a single resolvable band of this type.

The MLCT trends observed within this series of complexes mirror those found in related chromophores.[4c,d] The MLCT band of the Medap$^+$ complex in **2** is slightly blue-shifted with respect to that of its MeQ$^+$ counterpart in **1**, whilst the addition of a *trans*-CH=CH unit (in **3**) leads to a slight red-shift when compared with **1**. For the 4,4′-bipyridinium series, the MLCT energy decreases as L^A changes in the order MeQ$^+$ > PhQ$^+$ > 4-AcPhQ$^+$ > 2-PymQ$^+$, due to the steadily increasing acceptor strength of L^A. A small red-shift in the MLCT band is also observed on moving from L^A = PhQ$^+$ (in **4**) to Phbpe$^+$ (in **5**), and the latter also has a considerably lower MLCT energy than its Mebpe$^+$ counterpart in **3**. The main point of interest here is comparison of the MLCT spectra for **1**–**7** with those of previously reported salts with different L ligands (Fig. 1, Table 3).[4a,c,d]
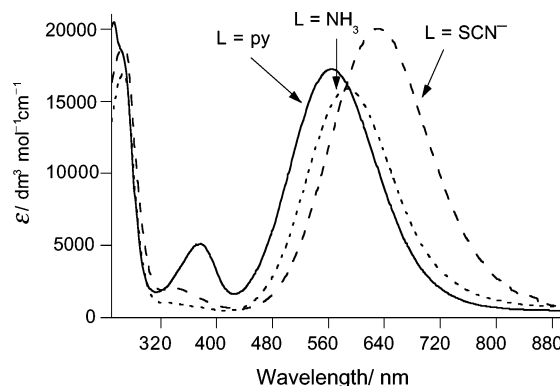
Fig. 1 UV/VIS absorption spectra of the salts *trans*-[Ru^{II}(NH$_3$)$_4$L-(MeQ$^+$)][PF$_6$]$_n$ (n = 2, L = NCS$^-$ (**1**); n = 3, L = pyridine (py) or NH$_3$) at room temperature in acetonitrile.

The MLCT bands in **1**–**7** are found to lower energies when compared with those of the other related complexes. Furthermore, a consistent trend is observed irrespective of the nature of L^A, *i.e.* the MLCT E_{max} increases in the order L = NCS$^-$ < dmap < mim < NH$_3$ < py (although the complete series is only

Table 2 UV/VIS, Stark spectroscopic and hyper-Rayleigh scattering data for the salts *trans*-[Ru^{II}(NCS)(NH$_3$)$_4$(L^A)][PF$_6$]$_2$

Salt	L^A	λ_{max}[a]/nm	E_{max}[a]/eV	f_{os}[a]	μ_{12}[b]/D	$\Delta\mu_{12}$[c]/D	$\Delta\mu_{ab}$[d]/D	c_b^2[e]	H_{ab}[f]/cm^{-1}	β_0[S][g]/10^{-30} esu	β_{1064}[h]/10^{-30} esu	β_0[H][i]/10^{-30} esu
1	MeQ$^+$	664	1.87	0.44	7.9	16.2	22.6	0.14	5200	335	963	247
2	Medap$^+$	656	1.89	0.29	6.4	15.0	19.8	0.12	4900	202	656	158
3	Mebpe$^+$	678	1.83	0.46[j]	8.0	20.4	26.0	0.11	4600	458	844	237
4	PhQ$^+$	714	1.74	0.39	7.7	17.2	23.0	0.13	4700	390	957	343
5	Phbpe$^+$	739	1.68	0.40	7.9	21.4	26.6	0.10	4000	553	1399	513
6	4-AcPhQ$^+$	734	1.69	0.47[j]	8.6	18.8	25.5	0.13	4600	569	998	398
7	2-PymQ$^+$	798	1.55	0.33	7.5	15.3	21.4	0.14	4400	412	832	399

[a] Measured in butyronitrile glasses at 77 K. [b] Calculated from eqn. (2). [c] Calculated from $f_{int}\Delta\mu_{12}$ using f_{int} = 1.33. [d] Calculated from eqn. (1). [e] Calculated from eqn. (3). [f] Calculated from eqn. (4). [g] Calculated from eqn. (5). [h] Obtained from 1064 nm HRS measurements in acetonitrile solutions at 298 K. [i] Derived from β_{1064} by application of the two-state model.[3] [j] At 298 K (value determined at 77 K unreasonably low; significant temperature dependance not expected).

available for L^A = MeQ$^+$). This trend is obviously consistent with the expectation that thiocyanate is the strongest electron donor amongst the ligands studied, and it therefore causes the largest destabilisation of the Ru^{II}-based HOMO.

Electrochemical studies

The new complex salts **1**–**7** were studied by cyclic voltammetry in acetonitrile and the results are presented in Table 1. All of the complexes exhibit reversible or quasi-reversible Ru$^{III/II}$ oxidation waves, together with L^A-based reduction processes which are reversible only for the complexes of MeQ$^+$ (in **1**), PhQ$^+$ (in **4**) or 4-AcPhQ$^+$ (in **6**).

As with the MLCT data, the trends observed in the redox behaviour within this new series of complexes are similar to those found in related chromophores.[4c,d] The Ru$^{III/II}$ $E_{1/2}$ values are indistinguishable in all cases except for **3** and **5**; the *ca.* –50 mV relative shifts in the latter being due to the mildly electron-donating character of the ethylene units. The steady red-shifting of the MLCT bands for the 4,4′-bipyridinium series hence arises purely from progressive stabilisation of the L^A-based LUMOs, and this is confirmed by the ligand reduction potentials. Again, comparison of the electrochemical data for **1**–**7** with those of previously reported salts with different L ligands (Fig. 2, Table 3)[4a,c,d] is instructive. As expected, the L^A reduction potentials show relatively little sensitivity to variations in L, and no clear trend is evident. However, the Ru$^{III/II}$ potentials show a more marked and consistent dependence on the nature of L. With a given L^A, the Ru$^{III/II}$ $E_{1/2}$ values decrease in the L order py > mim ≈ NH$_3$ ≈ dmap > NCS$^-$, reflecting the HOMO destabilization indicated by the MLCT data (see earlier). The average cathodic shift in the Ru$^{III/II}$ potential ($\Delta E_{1/2}$) is *ca.* 115 mV on moving from L = NH$_3$ to NCS$^-$, which corresponds closely with that predicted from the Lever parameters (130 mV).[7] The fact that $\Delta E_{1/2}$ is very similar to the corresponding average red-shift in

the MLCT band (0.12 eV) is consistent with the observation that changes in L primarily alter the HOMO energy, whilst having less effect on that of the LUMO.

Hyper-Rayleigh scattering studies

The β values of **1**–**7** were measured in acetonitrile solutions by using the HRS technique[8] with a 1064 nm Nd:YAG laser fundamental. Estimated static hyperpolarizabilities β_0[H] were obtained by application of the two-state model,[3] and the results are given in Table 2.

All of the new complexes show very large β_0[H] values, and these reveal trends which reinforce those observed previously in related complex salts.[4c,d] The primary trend is that β_0[H] increases in the order L^A = MeQ$^+$ < PhQ$^+$ ≤ 4-AcPhQ$^+$ ≈ 2-PymQ$^+$, attributable to the steadily increasing acceptor strength of L^A which is also revealed in the MLCT and electrochemical data. Although the latter clearly show that 2-PymQ$^+$ is the strongest electron acceptor of the 4,4′-bipyridinium ligands studied (see earlier), the β_0[H] values of **6** and **7** are effectively identical. Such apparently anomalous behaviour has been noted previously, and was ascribed to the extra conjugation imparted by a 4-acetyl group.[4d] The larger $\Delta\mu_{12}$ value of **6** when compared with **7** (see below) is consistent with this hypothesis. Also, β_0[H] decreases substantially on moving from L^A = MeQ$^+$ to Medap$^+$ (**1**→**2**), confirming that fixing the coplanarity of the 4,4′-bipyridinium rings has a deleterious effect on the quadratic NLO response.[4d,e] The β_0-enhancing effect of *N*-arylation is also clearly seen in moving from L^A = Mebpe$^+$ to Phbpe$^+$ (**3**→**5**). The β_0[H] values for **1** and **3** show no significant change on conjugation extension, whilst a relatively large increase is observed for the analogous *N*-Ph pair (**4**→**5**).

Stark spectroscopic studies

The new complex salts **1**–**7** were studied by Stark spectroscopy in butyronitrile glasses at 77 K and the results are presented in Table 2. As found previously with related Ru^{II} ammine complexes,[4e,13] the electroabsorption spectra of **1**–**7** were successfully modelled in terms of a large second derivative term, a small first derivative component and a negligible zeroth derivative contribution.

In all cases, the MLCT bands undergo marked red-shifts in the 77 K glass, as observed previously in related compounds.[4e,13] The μ_{12} values do not show any clear trend, but $\Delta\mu_{12}$ increases on replacing an *N*-Me (in **1**) with an *N*-Ph (in **4**) or *N*-(4-AcPh) (in **6**) substituent. Also, relatively large increases in $\Delta\mu_{12}$ are observed on extension of the conjugated system in **1** or **4**, in keeping with well established principles for dipolar CT chromophores. The $\Delta\mu_{ab}$ values are considerably larger than their adiabatic counterparts, also as observed in related compounds.[4e] The magnitude of c_b^2 reflects the degree of mixing between the diabatic states, and the observed values of *ca.* 0.1

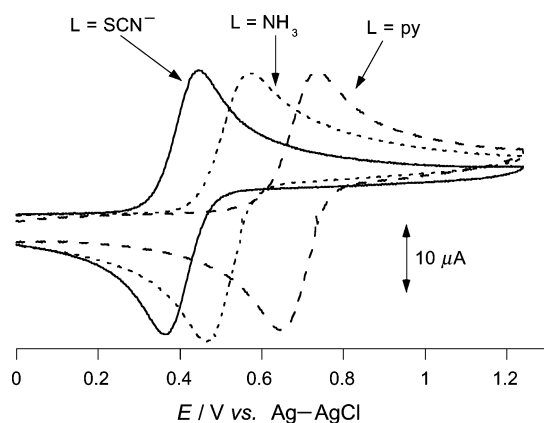
Fig. 2 Cyclic voltammograms showing the Ru$^{III/II}$ waves for the salts *trans*-[Ru^{II}(NH$_3$)$_4$L(MeQ$^+$)][PF$_6$]$_n$ (*n* = 2, L = NCS$^-$ (**1**); *n* = 3, L = py or NH$_3$) at room temperature in acetonitrile.

Table 3 Electrochemical, UV/VIS, Stark spectroscopic and hyper-Rayleigh scattering data for the salts *trans*-[Ru^{II}(NH$_3$)$_4$L(L^A)][PF$_6$]$_n$

Salt	L	L^A	n	$E_{1/2}$/V (*vs.* Ag–AgCl) [Ru$^{III/II}$]	L$^{+/0\,a}$	$\lambda_{max}{}^b$/nm	$E_{max}{}^b$/eV	μ_{12}/D	$\Delta\mu_{12}$/D	β_0[S]/10^{-30} esu	β_0[H]/10^{-30} esu
1	SCN⁻	MeQ⁺	2	0.40	−0.84	628	1.97	7.9	16.2	335	247
c,d	dmap	MeQ⁺	3	0.51	−0.82	614	2.02	6.1	15.3	191	130
c,d	mim	MeQ⁺	3	0.52	−0.83	602	2.06	5.5	17.1	170	100
d,e	NH$_3$	MeQ⁺	3	0.51	−0.86	590	2.10	5.2	13.8	120	123
f	py	MeQ⁺	3	0.69	−0.81	566	2.16	6.1	16.2	171	85
2	SCN⁻	Medap⁺	2	0.41		622	1.99	6.4	15.0	202	158
g	mim	Medap⁺	3	0.56		593	2.09	–	–	–	126
d,g	NH$_3$	Medap⁺	3	0.55		581	2.13	4.8	14.1	98	89
g	py	Medap⁺	3	0.70		564	2.20	–	–	–	51
3	SCN⁻	Mebpe⁺	2	0.36		638	1.94	8.0	20.4	458	237
d,g	mim	Mebpe⁺	3	0.47		604	2.05	6.3	18.0	256	168
d,g	NH$_3$	Mebpe⁺	3	0.46		595	2.08	5.5	16.2	175	142
d,g	py	Mebpe⁺	3	0.65		563	2.20	6.0	19.3	218	78
4	SCN⁻	PhQ⁺	2	0.42	−0.66	672	1.85	7.7	17.2	390	343
d,e	dmap	PhQ⁺	3	0.51	−0.68	658	1.88	7.1	15.9	313	260
d,e,g	mim	PhQ⁺	3	0.51	−0.68	642	1.93	6.2	17.4	258	254
d,e	NH$_3$	PhQ⁺	3	0.51	−0.70	628	1.97	5.7	15.3	186	220
5	SCN⁻	Phbpe⁺	2	0.35		676	1.83	7.9	21.4	553	513
d,g	mim	Phbpe⁺	3	0.48		638	1.93	6.5	20.2	352	310
d,g	NH$_3$	Phbpe⁺	3	0.47		628	1.97	5.7	19.5	249	192
d,g	py	Phbpe⁺	3	0.66		591	2.10	6.2	20.6	269	151
6	SCN⁻	4-AcPhQ⁺	2	0.41	−0.59	692	1.79	8.6	18.8	569	398
d,e	dmap	4-AcPhQ⁺	3	0.52	−0.58	688	1.80	6.8	20.3	388	410
d,e	mim	4-AcPhQ⁺	3	0.53	−0.58	666	1.86	6.4	16.8	279	332
d,e	NH$_3$	4-AcPhQ⁺	3	0.52	−0.59	654	1.90	5.8	17.0	229	354
7	SCN⁻	2-PymQ⁺	2	0.42		738	1.68	7.5	15.3	412	399
d,g	mim	2-PymQ⁺	3	0.57		698	1.78	6.4	16.8	323	336
g	NH$_3$	2-PymQ⁺	3	0.54		673	1.84	–	–	–	230
d,g	py	2-PymQ⁺	3	0.72		644	1.93	6.5	12.4	200	228

dmap = 4-(dimethylamino)pyridine, mim = *N*-methylimidazole, py = pyridine. *^{a}* Data is given only in cases where the reduction is electrochemically reversible. *^{b}* In acetonitrile solutions at 298 K. *^{c}* Ref 4*a*. *^{d}* Ref 4*e*. *^{e}* Ref 4*c*. *^{f}* Results to be published. *^{g}* Ref 4*d*.

are indicative of a limited degree of delocalization, consistent with the assignment of the visible absorptions as arising from MLCT processes. Both the $c_b{}^2$ and H_{ab} values found for **1**–**7** are similar to those for related complex chromophores.[4e] The β_0 values calculated from the Stark data by using eqn. (5) are also given in Table 2. These β_0[S] values are of similar magnitude, but generally somewhat larger than those derived from the HRS measurements. Because other two-state equations are available which would change the calculated β_0[S] values by constant factors of either 2 or 0.5,[15] direct comparison between the two sets of β_0 data is of limited use. However, the trends shown in β_0[S] are generally the same as those found in the HRS results, with the following exceptions: (i) **6** has the largest β_0 value according to the Stark data, but **5** has the largest β_0 derived from HRS and (ii) the Stark results indicate that conjugation extension leads to increases in β_0 of *ca.* 40% for *both* pairs **1/3** and **4/5**. The latter observation is consistent with results reported previously.[4e]

Static first hyperpolarizabilities: comparisons with previously published data

The collected data in Table 3 show that the new salts **1**–**7** all have larger β_0 values than any of their counterparts containing neutral L ligands (with the sole possible exception of the β_0[H] for **6**). These increases in β_0 can be traced to smaller E_{max} and larger μ_{12} values, whilst $\Delta\mu_{12}$ shows no consistent trend. The actual enhancement in β_0 varies considerably with L^A; based on the average increase shown by the two sets of data, **1** exhibits the largest increase when compared with its mim analogue (*ca.* 120%), whilst **7** shows the smallest (*ca.* 25%). The corresponding increases for the other five complexes lie in the range *ca.* 40–65%.

Conclusion

MLCT absorption and electrochemical data show that a *trans*-{Ru^{II}(NCS)(NH$_3$)$_4$}$^+$ centre is a stronger electron donor group than analogous units containing only neutral ligands. HRS and Stark spectroscopic studies confirm that this increased donor ability translates into enhanced β_0 responses, although the magnitude of the observed increase with respect to the analogous mim complexes varies over a range of *ca.* 25–120% with the nature of the pyridinium electron acceptor ligand. It can hence be anticipated that the coordination of more strongly electron-donating anions will lead to further, possibly dramatic, improvements in the quadratic NLO properties of dipolar *trans*-{Ru^{II}(NH$_3$)$_4$}$^{2+}$ complex chromophores. However, such increases may be achieved at the expense of decreased stability with respect to oxidation to Ru^{III} species.

Acknowledgements

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