

Syntheses, spectroscopic and molecular quadratic nonlinear optical properties of dipolar ruthenium(II) complexes of the ligand 1,2-phenylenebis(dimethylarsine)

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Six new complex salts *trans*-[Ru^{II}Cl(pdma)₂L][PF₆]_n [pdma = 1,2-phenylenebis(dimethylarsine); L = (*E,E,E*)-1,6-bis(4-pyridyl)hexa-1,3,5-triene (bph), *n* = 1, **5**; L = *N*-methyl-4-[(*E*)-2-(4-pyridyl)ethenyl]pyridinium (Mebpe⁺), *n* = 2, **7**; L = *N*-methyl-4-[(*E,E*)-4-(4-pyridyl)buta-1,3-dienyl]pyridinium (Mebpb⁺), *n* = 2, **8**; L = *N*-methyl-4-[(*E,E,E*)-6-(4-pyridyl)hexa-1,3,5-trienyl]pyridinium (Mebph⁺), *n* = 2, **9**; L = bis(4-pyridyl)acetylene (bpa), *n* = 1, **10**; L = *N*-methyl-4-[2-(4-pyridyl)ethynyl]pyridinium (Mebpa⁺), *n* = 2, **11**] have been prepared. The electronic absorption spectra of **5** and **7–11** display intense, visible metal-to-ligand charge-transfer (MLCT) bands, with λ_{max} values in the range 434–492 nm in acetonitrile. Cyclic voltammetric studies reveal reversible Ru^{III/II} waves with $E_{1/2}$ values in the range 1.06–1.15 V vs. Ag–AgCl, together with irreversible L-based reduction processes. Along with a number of previously reported related compounds (B. J. Coe *et al.*, *J. Chem. Soc., Dalton Trans.*, 1996, 3917; 1997, 591; 2000, 797), salts **5** and **7–11** have been investigated by using Stark (electroabsorption) spectroscopy in butyronitrile glasses at 77 K. These studies have afforded dipole moment changes $\Delta\mu_{12}$ for the MLCT transitions which have been used to calculate molecular static first hyperpolarizabilities β_0 according to the two-state equation $\beta_0 = 3\Delta\mu_{12}(\mu_{12})^2/(E_{\text{max}})^2$ (μ_{12} = transition dipole moment, E_{max} = MLCT energy). MLCT absorption and electrochemical data show that a *trans*-{Ru^{II}Cl(pdma)₂}⁺ centre is considerably less electron-rich than a {Ru^{II}(NH₃)₅}²⁺ unit. Although the β_0 responses of the pdma complexes are only a little smaller than those of their {Ru^{II}(NH₃)₅}²⁺ analogues, this result is partly attributable to unexpected changes in the relative μ_{12} values on freezing. Thus, substantial increases in μ_{12} for the arsine compounds act to partially offset the β_0 -decreasing influence of their higher E_{max} values when compared with the analogous pentaammine species. Single crystal X-ray structures have been obtained for the salts 1:2.5MeCN, 4:2MeCN, **7** and **11**, but only 1:2.5MeCN adopts a non-centrosymmetric space group (*Fdd2*) such as may show bulk NLO effects.

Introduction

Future optoelectronic and photonic data processing devices are likely to be based on molecular materials which exhibit nonlinear optical (NLO) properties.¹ Fundamental research into such materials has recently increasingly involved organotransition metal complexes which can display very marked NLO effects, combined with various other potentially useful properties such as redox and/or magnetic behaviour.² The establishment of detailed structure–activity correlations for first hyperpolarizabilities β , which govern quadratic molecular NLO effects, is the primary objective of most current work with such metal-based chromophores. Our contribution to this field has focused on hyper-Rayleigh scattering (HRS)³ and electronic Stark effect (electroabsorption)⁴ spectroscopic studies with various Ru^{II} pyridyl ammine complexes of pyridinium-substituted ligands.⁵ We have found that such dipolar chromophores can exhibit very large static first hyperpolarizabilities β_0 that are associated with intense, low energy metal-to-ligand charge-transfer (MLCT) transitions.⁵ The MLCT absorption and NLO properties of these complexes can be tuned *via* changes in ligand structure, in general accordance with the widely used two-state model,⁶ and can also be readily and reversibly switched by exploiting the Ru^{III/II} redox couple.⁷

Because of continual difficulties with growing single crystals suitable for X-ray diffraction studies, we have obtained only scant structural information on our Ru^{II} ammine complexes.^{5a,c,d} Inspired by earlier studies involving complexes of the chelating ligand 1,2-phenylenebis(dimethylarsine) (pdma),⁸ we have prepared a series of complexes in which *trans*-{Ru^{II}Cl(pdma)₂}⁺ centres are coor-

dated to pyridinium ligands, with the original primary objective of gaining detailed crystallographic data. The syntheses, properties and crystal structures of some of these complexes have been previously reported,⁹ but without any accompanying NLO data. Such data was originally not obtained for the following reasons: (i) MLCT absorption and electrochemical studies clearly show that a *trans*-{Ru^{II}Cl(pdma)₂}⁺ centre is a rather less effective electron donor when compared with an ammine-bearing unit such as {Ru^{II}(NH₃)₅}²⁺, suggesting that the β values of the pdma complexes will be smaller than those of their ammine analogues; (ii) the MLCT bands of the pdma complexes are found very close to 532 nm, precluding the acquisition of meaningful HRS data when using the standard 1064 nm Nd³⁺-YAG laser fundamental with which the ammine complexes have been investigated. However, since this previous study was reported,⁹ we have carried out Stark spectroscopic experiments with our ammine complexes and found that this technique is a useful approach to deriving β values for such chromophores.^{5e–i} Although the Stark approach is indirect, the resonance effects which often limit the utility of direct HRS measurements can be discounted. We have therefore now synthesised some further new dipolar Ru^{II} pdma complexes to expand the existing series, and investigated these compounds by using Stark spectroscopy.

Experimental

Materials and procedures

The compound pdma was obtained from Dr G. Reid, University of Southampton. (*E,E,E*)-1,6-Bis(4-pyridyl)hexa-1,3,5-triene

(bph)¹⁰ and the salts *trans*-[Ru^{II}Cl(pdma)₂(NO)][PF₆]₂,¹¹ *N*-methyl-4-[(*E*)-2-(4-pyridyl)ethenyl]pyridinium hexafluorophosphate ([Mebpe⁺]PF₆)^{5d} and *N*-methyl-4-[(*E,E*)-4-(4-pyridyl)buta-1,3-dienyl]pyridinium hexafluorophosphate ([Mebpb⁺]PF₆)⁵ⁱ were prepared according to published procedures. The compound bis(4-pyridyl)acetylene (bpa) was prepared *via* modification of a literature procedure,¹² with chromatographic purification resulting in improved yields. All other reagents were obtained commercially and used as supplied. All reactions were conducted under an argon atmosphere. Products were dried at room temperature in a vacuum desiccator (CaSO₄) for *ca.* 24 h prior to characterization.

General physical measurements

Proton NMR spectra were recorded on a Varian Gemini 200 spectrometer and all shifts are referenced to SiMe₄. 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. Mass spectra were recorded using +electrospray on a Micromass Platform spectrometer (cone voltage 80 V), with the exception of compound **8** for which the MALDI technique was used.

Cyclic voltammetric measurements were carried out with an EG&G PAR model 283 potentiostat/galvanostat. An EG&G PAR K0264 single compartment microcell was used with a Ag–AgCl reference electrode (3 mol dm⁻³ NaCl, saturated AgCl), a platinum-disc working electrode and platinum-wire auxiliary electrode. Acetonitrile (HPLC grade) was distilled before use and tetra-*n*-butylammonium hexafluorophosphate, twice recrystallized from ethanol and dried *in vacuo*, was used as supporting electrolyte. Solutions containing *ca.* 10⁻³ mol dm⁻³ analyte (0.1 mol dm⁻³ electrolyte) were deaerated by purging with N₂. All *E*_{1/2} values were calculated from (*E*_{pa} + *E*_{pc})/2 at a scan rate of 200 mV s⁻¹.

Syntheses

Bis(4-pyridyl)acetylene. CAUTION: This compound has been reported to cause painful blistering of the skin several days after contact; use gloves when handling. Br₂ (3.5 cm³, 10.8 g, 68 mmol) was added dropwise to a stirred solution of *trans*-1,2-bis(4-pyridyl)ethylene (3.52 g, 19.3 mmol) in HBr (48%, 46.5 cm³) at 0 °C. The mixture was stirred at 120 °C for 2 h, then cooled to room temperature. Chilling in ice caused the precipitation of an orange solid which was filtered off and washed with water then stirred in aqueous NaOH (2 mol dm⁻³, 120 cm³) for 30 min. The resulting white solid, 1,2-dibromo-1,2-bis(4-pyridyl)ethane, was filtered off, washed with a large amount of water and dried: yield 4.0 g (61%). δ_H (CDCl₃) 8.69 (4 H, d, *J* 5.9, C₅H₄N), 7.39 (4 H, d, *J* 5.9, C₅H₄N), 5.27 (2 H, s, CH). Finely cut Na (1.2 g, 52 mmol) was stirred in *t*-BuOH (120 cm³) at 80 °C under argon until dissolution was complete (overnight). 1,2-Dibromo-1,2-bis(4-pyridyl)ethane (4.0 g, 11.7 mmol) was added in portions and the mixture was stirred under argon at 80 °C for 4 h. The mixture was cooled to 40 °C and EtOH was added (20 cm³), followed by water (20 cm³, CAUTION!). The brown solution was extracted with CHCl₃ until the extracts became colourless (*ca.* 6 × 50 cm³), the extracts dried (CaCl₂), and evaporated to dryness. The solid was dissolved in a minimum volume of CHCl₃, loaded onto a silica gel column (200 g), and eluted with diethyl ether–THF (85 : 15). The major band was collected and evaporated to afford a white solid: yield 2.0 g (95%). δ_H (CDCl₃) 8.60 (4 H, d, *J* 6.0, C₅H₄N), 7.35 (4 H, d, *J* 6.0, C₅H₄N) (Found: C, 79.92; H, 4.42; N, 15.31. Calc. for C₁₂H₈N₂: C, 79.98; H, 4.47; N, 15.54%).

***trans*-[Ru^{II}Cl(pdma)₂(bph)]PF₆ 5.** A solution of *trans*-[Ru^{II}Cl(pdma)₂(NO)][PF₆]₂ (125 mg, 0.122 mmol) and NaN₃ (8.1 mg, 0.125 mmol) in acetone (10 cm³) was stirred at room temperature for 2 h. Butan-2-one (10 cm³) and bph (286 mg, 1.22 mmol) were

added and the acetone removed *in vacuo*. The solution was heated under reflux for 2 h, cooled to room temperature, and diethyl ether was added to afford a dark red–orange precipitate. This solid was filtered off and the excess bph was removed by two reprecipitations from acetone–diethyl ether. The product was further purified by precipitation from acetone–aqueous NH₄PF₆, then acetone–diethyl ether to afford a brick-red solid. Recrystallization from acetonitrile–diethyl ether afforded a dark red solid: yield 47 mg (35%). δ_H (CD₃COCD₃) 8.51 (2 H, d, *J* 7.2, C₅H₄N), 8.32 (4 H, m, 2C₆H₂), 7.84 (4 H, m, 2C₆H₂), 7.53 (2 H, d, *J* 6.7, C₅H₄N), 7.42 (2 H, d, *J* 7.3, C₅H₄N), 7.31–7.13 (2 H, m, 2CH), 7.09 (2 H, d, *J* 6.7, C₅H₄N), 6.75–6.66 (3 H, m, 3CH), 6.52 (1 H, d, *J* 15.5, CH), 1.90 (12 H, s, 4AsMe), 1.78 (12 H, s, 4AsMe) (Found: C, 39.14; H, 4.06; N, 2.57. Calc. for C₃₆H₄₆N₂As₄ClF₆PRu: C, 39.74; H, 4.26; N, 2.57%). *m/z*: 943 ([M – PF₆]⁺).

***trans*-[Ru^{II}Cl(pdma)₂(Mebpe⁺)]PF₆ 7.** This was prepared and purified in an identical fashion to **5** by using *trans*-[Ru^{II}Cl(pdma)₂(NO)][PF₆]₂ (75 mg, 0.073 mmol), NaN₃ (4.9 mg, 0.075 mmol) in acetone (5 cm³) and [Mebpe⁺]PF₆ (125 mg, 0.365 mmol) in place of bph. The product was obtained as dark red needles: yield 43 mg (49%). δ_H (CD₃COCD₃) 8.91 (2 H, d, *J* 6.9, C₅H₄N), 8.31 (4 H, m, 2C₆H₂), 8.22 (2 H, d, *J* 6.9, C₅H₄N), 7.84 (4 H, m, 2C₆H₂), 7.76–7.58 (4 H, m, 2CH, C₅H₄N), 7.32 (2 H, d, *J* 6.7, C₅H₄N), 4.48 (3 H, s, C₅H₄N–Me) 1.91 (12 H, s, 4AsMe), 1.79 (12 H, s, 4AsMe) (Found: C, 33.71; H, 3.63; N, 2.30. Calc. for C₃₃H₄₅As₄ClF₁₂N₂P₂Ru: C, 33.14; H, 3.79; N, 2.34%). *m/z*: 1050 ([M – PF₆]⁺).

***trans*-[Ru^{II}Cl(pdma)₂(Mebpb⁺)]PF₆ 8.** This was prepared and purified in an identical fashion to **7**, but using [Mebpb⁺]PF₆ (134 mg, 0.364 mmol) in place of [Mebpe⁺]PF₆. Dark red needles were obtained: yield 53 mg (59%). δ_H (CD₃COCD₃) 8.52 (2 H, d, *J* 6.7, C₅H₄N), 8.29 (4 H, m, 2C₆H₂), 7.98 (2 H, d, *J* 6.9, C₅H₄N), 7.91 (4 H, m, 2C₆H₂), 7.61–7.52 (1 H, m, CH), 7.43 (2 H, d, *J* 6.7, C₅H₄N), 7.28–7.19 (1 H, m, CH), 6.99 (2 H, d, *J* 6.6, C₅H₄N), 6.86 (2 H, m, 2CH), 4.28 (3 H, s, C₅H₄N–Me), 1.91 (12 H, s, 4AsMe), 1.73 (12 H, s, 4AsMe) (Found: C, 34.33; H, 3.56; N, 2.32. Calc. for C₃₅H₄₇As₄ClF₁₂N₂P₂Ru: C, 34.40; H, 3.88; N, 2.29%). *m/z*: 932 ([M – 2PF₆]⁺).

***trans*-[Ru^{II}Cl(pdma)₂(Mebph⁺)]PF₆ 9.** A solution of **5** (50 mg, 0.046 mmol) in DMF (1.5 cm³) and methyl iodide (0.5 cm³) was stirred for 24 h at room temperature. The excess methyl iodide was removed *in vacuo* and addition of aqueous NH₄PF₆ to the dark red solution gave a brick-red precipitate which was filtered off, washed with water and dried. Purification was effected by precipitation from acetone–diethyl ether: yield 48 mg (84%). δ_H (CD₃COCD₃) 8.84 (2 H, d, *J* 6.9, C₅H₄N), 8.32 (4 H, m, 2C₆H₂), 8.14 (2 H, d, *J* 6.7, C₅H₄N), 7.88 (4 H, m, 2C₆H₂), 7.74–7.66 (1 H, m, CH), 7.53 (2 H, d, *J* 6.9, C₅H₄N), 7.27–7.18 (1 H, m, CH), 7.12 (2 H, d, *J* 6.9, C₅H₄N), 6.96 (1 H, d, *J* 15.5, CH), 6.89–6.74 (2 H, m, 2CH), 6.66 (1 H, d, *J* 15.7, CH), 4.48 (3 H, s, C₅H₄N–Me), 1.90 (12 H, s, 4AsMe), 1.78 (12 H, s, 4AsMe) (Found: C, 35.59; H, 3.50; N, 2.25. Calc. for C₃₇H₄₉As₄ClF₁₂N₂P₂Ru: C, 35.61; H, 3.96; N, 2.24%). *m/z*: 1102 ([M – PF₆]⁺).

***trans*-[RuCl(pdma)₂(bpa)]PF₆ 10.** This was prepared and purified in an identical fashion to **5** by using bpa (221 mg, 1.23 mmol) in place of bph. The product was obtained as a red–brown solid: yield 79 mg (63%). δ_H (CD₃COCD₃) 8.70 (2 H, br s, C₅H₄N), 8.30 (4 H, m, 2C₆H₂), 7.83 (4 H, m, 2C₆H₂), 7.77 (2 H, d, *J* 6.7, C₅H₄N), 7.50 (2 H, d, *J* 6.6, C₅H₄N), 7.19 (2 H, d, *J* 6.7, C₅H₄N), 1.90 (12 H, s, 4AsMe), 1.80 (12 H, s, 4AsMe) (Found: C, 36.81; H, 3.72; N, 2.67. Calc. for C₃₂H₄₀As₄ClF₆N₂PRu: C, 37.18; H, 3.90; N 2.71%). *m/z*: 888 ([M – PF₆]⁺).

***trans*-[Ru^{II}Cl(pdma)₂(Mebpa⁺)]PF₆ 11.** This was prepared and purified in an identical fashion to **9** by using **10** (50 mg, 0.048 mmol) in place of **5**. The product was obtained as a dark red solid: yield 53 mg (92%). δ_H (CD₃COCD₃) 9.06 (2 H, d, *J* 6.7,

Table 1 Crystallographic data and refinement details for complex salts **1**·2.5MeCN, **4**·2MeCN, **7** and **11**

	1 ·2.5MeCN	4 ·2MeCN	7	11
Formula	C ₂₉ H _{43.50} As ₄ ClF ₆ N _{4.50} PRu	C ₃₆ H ₄₈ As ₄ ClF ₆ N ₄ PRu	C ₃₃ H ₄₅ As ₄ ClF ₁₂ N ₂ P ₂ Ru	C ₃₃ H ₄₃ As ₄ ClF ₉ N ₂ P _{1.50} Ru
<i>M</i>	1036.35	1117.95	1195.85	1121.35
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Monoclinic
Space group	<i>Fdd2</i>	<i>P2₁/n</i>	<i>P2₁/c</i>	<i>P2₁/c</i>
<i>a</i> /Å	21.9898(5)	12.2140(3)	20.4769(2)	20.2299(11)
<i>b</i> /Å	43.4293(11)	13.1090(4)	9.44240(10)	9.5405(4)
<i>c</i> /Å	16.3636(4)	26.6750(6)	24.6388(3)	24.5138(14)
β /°		90.7850(13)	112.9200(10)	112.535(2)
<i>U</i> /Å ³	15627.3(7)	4270.62(19)	4387.82(8)	4370.0(4)
<i>Z</i>	16	4	4	4
<i>T</i> /K	120(2)	120(2)	120(2)	120(2)
μ /mm ⁻¹	3.928	3.600	3.563	3.544
Reflections collected	35833	37632	14172	28451
Independent reflections (<i>R</i> _{int})	6876 (0.0936)	7489 (0.0656)	7731 (0.0221)	8355 (0.0774)
Final <i>R</i> 1, <i>wR</i> 2 [<i>I</i> > 2 σ (<i>I</i>)] ^a	0.0443, 0.1086	0.0392, 0.0895	0.0558, 0.1564	0.0527, 0.1243
(all data)	0.0509, 0.1131	0.0699, 0.1007	0.0617, 0.1628	0.0923, 0.1372

^aThe structures were refined on *F*_o² using all data; the values of *R*1 are given for comparison with older refinements based on *F*_o with a typical threshold of *F*_o > 4 σ (*F*_o).

C₅H₄N, 8.30 (4 H, m, 2C₆H₂), 8.21 (2 H, d, *J* 6.9, C₅H₄N), 7.83 (6 H, m, 2C₆H₂ and C₅H₄N), 7.26 (2 H, d, *J* 6.9, C₅H₄N), 4.57 (3 H, s, C₅H₄N-Me), 1.91 (12 H, s, 4AsMe), 1.85 (12 H, s, 4AsMe) (Found: C, 33.21; H, 3.26; N, 2.41. Calc. for C₃₃H₄₃As₄ClF₁₂N₂P₂Ru: C, 33.20; H, 3.63; N, 2.35%). *m/z*: 1048 ([M - PF₆⁻]⁺).

X-Ray structural determinations

Crystals of complex salts **1**·2.5MeCN, **4**·2MeCN, **7** and **11** were obtained by slow diffusion of diethyl ether vapour into acetonitrile solutions. The crystals chosen for diffraction studies had the following approximate dimensions and appearances: 0.20 × 0.10 × 0.08 mm, yellow block (**1**·2.5MeCN); 0.15 × 0.10 × 0.10 mm, orange rod (**4**·2MeCN); 0.60 × 0.40 × 0.20 mm, red block (**7**); 0.40 × 0.20 × 0.02 mm, dark red plate (**11**). The crystal of **11** contained unrefinable solvent (probably acetonitrile) which was removed by using the SQUEEZE procedure. Although **11** is a bis-hexafluorophosphate salt, the asymmetric unit contains 1.5 PF₆⁻ anions, with one being completed due to crystallographic symmetry, giving rise to F₉P_{1.5} in the crystallographic formula. Crystallographic data and refinement details are presented in Table 1.

CCDC reference numbers 240011 (**1**·2.5MeCN), 240012 (**4**·2MeCN), 240013 (**7**) and 240014 (**11**).

See <http://www.rsc.org/suppdata/dt/b4/b409432h/> for crystallographic data in CIF or other electronic format.

Stark spectroscopy

The Stark apparatus, experimental methods and data analysis procedure were exactly as previously reported,^{5e,13} with the only modification being that a Xe arc lamp was used as the light source in the place of a W filament bulb. Butyronitrile was used as the glassing medium, for which the local field correction *f*_{int} is estimated as 1.33.^{5e,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

$$\Delta\mu_{ab}^2 = \Delta\mu_{12}^2 + 4\mu_{12}^2 \quad (1)$$

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. Analysis of the Stark spectra in terms of the Liptay treatment⁴ affords $\Delta\mu_{12}$, and the transition dipole moment μ_{12} can be determined from the oscillator strength *f*_{os} of the transition by

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

where *E*_{max} is the energy of the MLCT maximum (in wavenumbers). The degree of delocalization *c*_b² and electronic coupling matrix element *H*_{ab} for the diabatic states are given by

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

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

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

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

Results and discussion

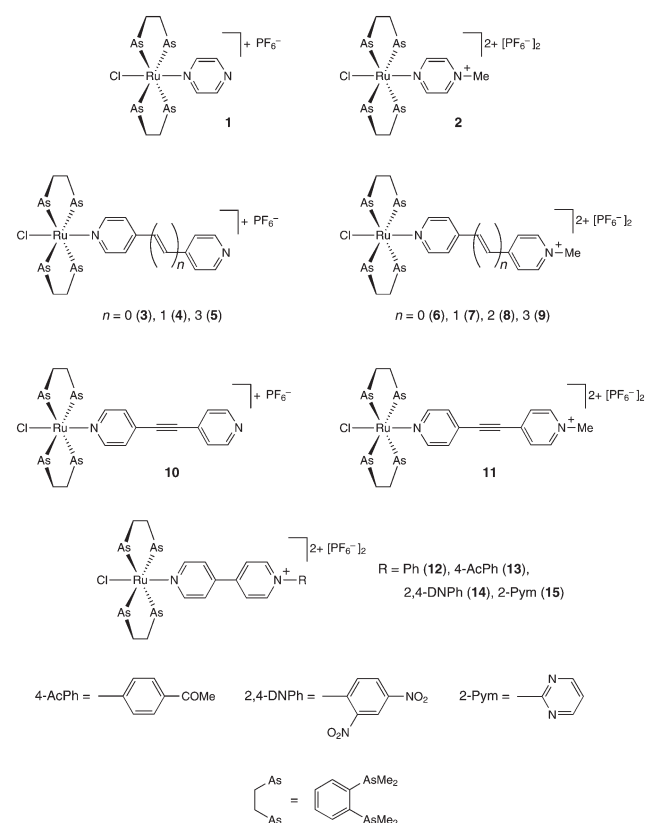


Table 2 UV/VIS and electrochemical data for complex salts **5** and **7–11** in acetonitrile

Complex salt	λ_{\max}/nm ($\epsilon_{\max}/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$)	E_{\max}^a/eV	Assignment	$E_{1/2}/\text{V}$ vs. Ag–AgCl ($\Delta E_p/\text{mV}$) ^b	
				$E_{1/2}[\text{Ru}^{\text{III}}]$	E_{pc}^c
5 <i>trans</i> -[Ru ^{II} Cl(pdma) ₂ (bph)]PF ₆	446 (18800)	2.78	d _π →π*	1.06 (90)	−1.07
	362 (37300)	3.43	π→π*		
7 <i>trans</i> -[Ru ^{II} Cl(pdma) ₂ (Mebpe ⁺)]PF ₆	492 (13000)	2.52	d _π →π*	1.10 (95)	−0.79
	316 (28500)	3.92	π→π*		
8 <i>trans</i> -[Ru ^{II} Cl(pdma) ₂ (Mebpb ⁺)]PF ₆	486 (15700)	2.53	d _π →π*	1.09 (105)	−0.80
	356 (37900)	3.48	π→π*		
9 <i>trans</i> -[Ru ^{II} Cl(pdma) ₂ (Mebph ⁺)]PF ₆	472 (15000)	2.58	d _π →π*	1.07 (110)	−0.80
	394 (26800)	3.15	π→π*		
10 <i>trans</i> -[RuCl(pdma) ₂ (bpa)]PF ₆	434 (6000)	2.86	d _π →π*	1.12 (95)	−1.10
	286 (22100)	4.33	π→π*		
11 <i>trans</i> -[Ru ^{II} Cl(pdma) ₂ (Mebpa ⁺)]PF ₆	488 (11500)	2.54	d _π →π*	1.15 (105)	−0.98
	300 (21900)	4.13	π→π*		

^a Solutions *ca.* 3–8 × 10^{−5} mol dm^{−3}. ^b Solutions *ca.* 10^{−3} mol dm^{−3} in analyte and 0.1 mol dm^{−3} in NBu₄PF₆ at a platinum disc working electrode with a scan rate of 200 mV s^{−1}. Ferrocene internal reference $E_{1/2} = 0.43$ V, $\Delta E_p = 90$ –110 mV. ^c For an irreversible reduction process.

Table 3 MLCT absorption and selected cyclic voltammetric data for complex salts **1–15** in acetonitrile

Complex salt	$\lambda_{\max}^a/\text{nm}$	E_{\max}^a/eV	$\epsilon^a/\text{mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$	E/V vs. Ag–AgCl ^b	
				$E_{1/2}[\text{Ru}^{\text{III}}]$	$E_{1/2}[\text{L}^{+/0}]$ or E_{pc}^c
1 ^d	422	2.94	6100	1.22	−1.48 ^e
2 ^d	558	2.22	12000	1.48	−0.35
3 ^e	418	2.97	8400	1.10	−1.49 ^e
4 ^e	434	2.86	14300	1.08	−1.33
5	446	2.78	18800	1.06	−1.07 ^e
6 ^f	486	2.55	8300	1.14	−0.74
7	492	2.52	13000	1.10	−0.79 ^e
8	486	2.53	15700	1.09	−0.80 ^e
9	472	2.58	15000	1.07	−0.80 ^e
10	434	2.86	6000	1.12	−1.10 ^e
11	488	2.54	11500	1.15	−0.98 ^e
12 ^f	510	2.43	12500	1.15	−0.58
13 ^f	520	2.38	10000	1.15	−0.51
14 ^f	536	2.31	10400	1.16	−0.38 ^e
15 ^f	544	2.28	10400	1.16	−0.34

^a Solutions *ca.* 3–8 × 10^{−5} M. ^b Solutions *ca.* 10^{−3} M in analyte and 0.1 M in NBu₄PF₆ at a platinum bead/disc working electrode with a scan rate of 200 mV s^{−1}. Ferrocene internal reference $E_{1/2} = 0.43$ V. ^c For an irreversible reduction process. ^d Ref. 8a. ^e Ref. 8b. ^f Ref. 9.

Synthetic studies

The new complex salts **5** and **7–11** were prepared in order to provide an extensive series of systematically modified compounds together with the existing **1–4**, **6**⁹ and **12–15**.⁹ The complexes in **5** and **10** were prepared *via* reactions of the neutral pro-ligands bph or bpa with the sodium azide-treated complex precursor *trans*-[Ru^{II}Cl(pdma)₂(NO)]²⁺,¹¹ and **7** and **8** were prepared similarly but using the pro-ligand salts of the appropriate *N*-methylated cations, *i.e.* [Mebpe⁺]PF₆ and [Mebpb⁺]PF₆, respectively. The complexes in **9** and **11** were synthesized *via* treatment of **5** and **10**, respectively, with methyl iodide. All of the new compounds show diagnostic proton NMR spectra, and mass spectra and elemental analyses provide further confirmation of identity and purity.

Electronic absorption spectroscopic studies

The UV/Visible absorption spectra of salts **5** and **7–11** have been measured in acetonitrile and the results are presented in Table 2. These spectra feature intense absorptions in the UV region due to π→π* intraligand charge-transfer (ILCT) transitions, together with intense, broad d_π(Ru^{II})→π*(L) (L = pyridyl ligand) visible MLCT bands. Data for the MLCT bands are also collected in Table 3 together with data for the other compounds studied in this work.^{8,9}

As expected, methylation of the uncoordinated pyridyl nitrogen in **1**, **3–5** or **10** (to give **2**, **6**, **7**, **9** or **11**, respectively) leads to large red-shifts in the MLCT bands (Tables 2 and 3). These red-shifts are accompanied by substantial increases in intensity for **1** and **10**. Within the polyene series **6–9**, an initial red-shift of the MLCT

band is observed on moving from *n* = 0 to 1, but the MLCT energy E_{\max} increases slightly as the chain is further extended up to three *E*-ethylene units (Table 3). This is very unusual optical behaviour because the intramolecular charge-transfer (ICT) bands of donor–acceptor polyene chromophores normally *red-shift* on elongation of conjugated chains, irrespective of whether terminal metal centres are present.¹⁴ To our knowledge, the only previous reports of donor–acceptor polyenes in which the ICT/MLCT bands blue-shift with increasing conjugation length involve compounds having tetrathiafulvalenyl donor groups with various strong electron acceptors including 2,2-dicyanovinyl,¹⁵ and also complexes related to **6–9**, but containing Ru^{II} ammine centres, which have recently been studied in our laboratory.^{5f,i}

Within the 4,4'-bipyridinium-based series **6** and **12–15**, E_{\max} decreases steadily as the *N*-pyridinium substituent changes in the order R = Me > Ph > 4-AcPh > 2,4-DNPh > 2-Pym (Table 3). Similar behaviour has also been observed in Ru^{II} ammine complexes of the same ligands,^{5c,d} and this trend is attributable primarily to a continual stabilisation of the ligand-based LUMO as the electron-withdrawing ability of R increases, as reflected in the ligand first reduction potentials (see below). Replacing a *trans*-CH=CH with a C≡C bridge does not significantly affect the MLCT energies, according to the data for the pairs **4/10** and **7/11**.

Electrochemical studies

The new complex salts **5** and **7–11** were studied by cyclic voltammetry in acetonitrile and the results are presented in Table 2. All of the complexes show reversible Ru^{III/II} oxidation waves, together

Table 4 MLCT absorption and Stark spectroscopic data for complex salts **1–4**, **6–9** and **11–15**^a

Salt	λ_{\max}/nm	E_{\max}/eV	f_{os}	μ_{12}^b/D	$\Delta\mu_{12}^c/\text{D}$	$\Delta\mu_{\text{ab}}^d/\text{D}$	c_b^{2e}	$H_{\text{ab}}/\text{cm}^{-1}$	$\beta_0^g/10^{-30}$ esu
1	424	2.92	0.10	3.0	8.2	10.2	0.10	7000	10
2	545	2.28	0.31	6.0	6.1	13.5	0.27	8200	50
3	422	2.94	0.21	4.3	11.1 ^h	14.0	0.11	7300	28
4	506	2.45	0.26	5.3	18.6	21.5	0.07	4900	100
6	491	2.53	0.41	6.6	14.3	19.4	0.13	6900	113
7	515	2.41	0.33	6.0	16.9	20.7	0.09	5600	123
8	506	2.45	0.94	10.0	20.6	28.7	0.14	6900	401
9	501	2.48	1.04	10.5	22.2	30.6	0.14	6900	468
11	509	2.44	0.38	6.4	18.2	22.3	0.09	5600	146
12	516	2.40	0.37	6.4	17.4	21.6	0.10	5700	144
13	525	2.36	0.41	6.7	17.9	22.4	0.10	5700	170
14	536	2.31	0.46	7.3	17.9	23.1	0.11	5900	206
15	544	2.28	0.53	7.8	19.7	25.1	0.11	5700	268

^a Measured in butyronitrile glasses at 77 K. ^b Calculated from eqn (2). ^c Calculated from $f_{\text{int}}\Delta\mu_{12}$ using $f_{\text{int}} = 1.33$. ^d Calculated from eqn (1). ^e Calculated from eqn (3). ^f Calculated from eqn (4). ^g Calculated from eqn (5). ^h Inferior data fit.

with irreversible pyridyl ligand-based reduction processes. Data for the Ru^{III/II} waves are also collected in Table 3 together with data for the other compounds studied in this work.^{8,9}

The large red-shifts in the MLCT bands caused by methylation of the uncoordinated pyridyl nitrogens in **1**, **3–5** or **10** (to give **2**, **6**, **7**, **9** or **11**, respectively) are shown by the electrochemical data to arise primarily from stabilisation of the ligand-based LUMOs. However, the Ru-based HOMOs also show some stabilisation, especially on moving from **1** to **2** in which the extent of electronic coupling between the pyridinium nitrogen and the Ru centre is expected to be the largest amongst the complexes studied. The corresponding changes in the Ru^{III/II} $E_{1/2}$ values in the $n = 1$ or 3 compounds are only small. Within the polyene series **6–9**, the Ru^{III/II} $E_{1/2}$ value decreases slightly on moving from $n = 0$ to 1, but subsequently shows smaller decreases. This observation can be ascribed to the lessening influence of the electron-withdrawing *N*-methylpyridinium group as the polyene chain extends. Replacing a *trans*-CH=CH with a C≡C bridge causes slight increases in the Ru^{III/II} $E_{1/2}$ values (see data for the pairs **4/10** and **7/11**), indicating that the Ru^{II} centres become less electron-rich. This effect can be attributed to decreased σ -donating and/or increased π -accepting ability of the pyridyl ligand.

Stark spectroscopic studies

We have studied complex salts **1–4**, **6–9** and **11–15** by using Stark spectroscopy in butyronitrile glasses at 77 K, and the results are presented in Table 4. Satisfactory data fits could only be obtained for the MLCT bands, and not for the high-energy ILCT bands of these compounds. As observed previously with Ru^{II} ammine complex salts,^{5e–i,13} the E_{\max} values generally decrease on moving from acetonitrile solution to butyronitrile glass (Tables 3 and 4), but an opposite effect is observed for **2**. Within the polyene series **6–9**, the $\Delta\mu_{12}$ values increase steadily with n , as is normal for donor–acceptor polyenes, whilst a large increase in μ_{12} is observed on moving from $n = 1$ to 2. It is reasonable to assume that the lowest energy (*i.e.* MLCT) electronic transitions will dominate the NLO responses of these chromophores, so β_0 values have been derived by using eqn. (5). The β_0 values for **6–9** appear to increase on moving from $n = 0$ to 3, but the large estimated relative errors ($\pm 20\%$) on these numbers mean that the values for the pairs **6/7** and **8/9** may not be significantly different.

As expected, increasing the ligand electron acceptor strength by *N*-methylation of **1**, **3** and **4** causes increases in β_0 , this effect being largest in the pyrazine complexes. The complex in **2** also has the largest values of c_b^{2e} and H_{ab} , consistent with this species having the greatest degree of delocalization and electronic coupling of those studied. The maximum possible value of c_b^{2e} (0.5) corresponds to essentially complete delocalization of the orbitals involved in the electronic transition. Such a situation has been observed for the visible absorption band ($\lambda_{\max} = 538$ nm at 298 K in 1 : 1 glycerol–water) of [Ru^{II}(NH₃)₅L][BF₄]₃ (L = *N*-methylpyrazinium), which is therefore best described as arising from a non-directional

π – π^* transition (this complex salt exhibits a true MLCT band at $\lambda_{\max} = 880$ nm at 298 K in 1 : 1 glycerol–water).¹³ Although the c_b^{2e} for **2** is smaller than that of its pentaammine analogue, it is still considerably larger than those for the other compounds studied, which at *ca.* 0.1, are consistent with MLCT processes. Within the 4,4'-bipyridinium-based series **6** and **12–15**, β_0 increases steadily, approximately doubling on replacement of a *N*-Me with a *N*-(2-Pym) substituent. As expected according to the two-state model, this trend parallels the red-shifting of the MLCT bands, and similar behaviour of β_0 has been observed in the related Ru^{II} ammine complexes of the same ligands.^{5c,d}

Structural studies

Having investigated the molecular quadratic NLO properties of complex salts **1–4**, **6–9** and **11–15**, the next steps towards potentially useful materials are the preparation and study of crystalline samples in which bulk NLO effects may be observed. We have obtained single crystal X-ray structures for 1·2.5MeCN, 4·2MeCN, **7** and **11**. Representations of the molecular structures of the complex cations are shown in Figs 1–4, respectively, and selected interatomic distances and angles are presented in Table 5.

The dihedral angles between the pyridyl rings are as follows: 5.21(23)° (4·2MeCN), 12.31(62)° (**7**) and 12.66(3)° (**11**), in each case consistent with significant electronic coupling throughout the conjugated ligand systems. The *ca.* 0.03 Å shortening of the Ru–N distance in **11** when compared with **7** can be attributed to a greater extent of π -back-bonding in the former due to the electron-withdrawing nature of the ethynyl unit, consistent with the electrochemical data. Unfortunately, although the cations in 4·2MeCN,

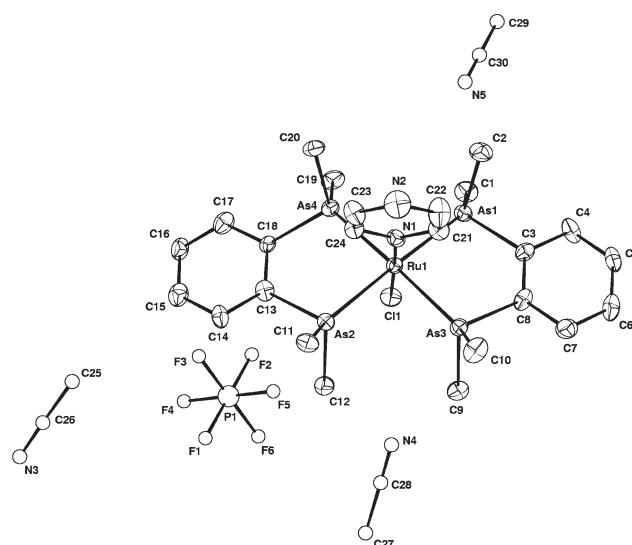


Fig. 1 Structural representation of the complex salt **1**·2.5MeCN (50% probability ellipsoids).

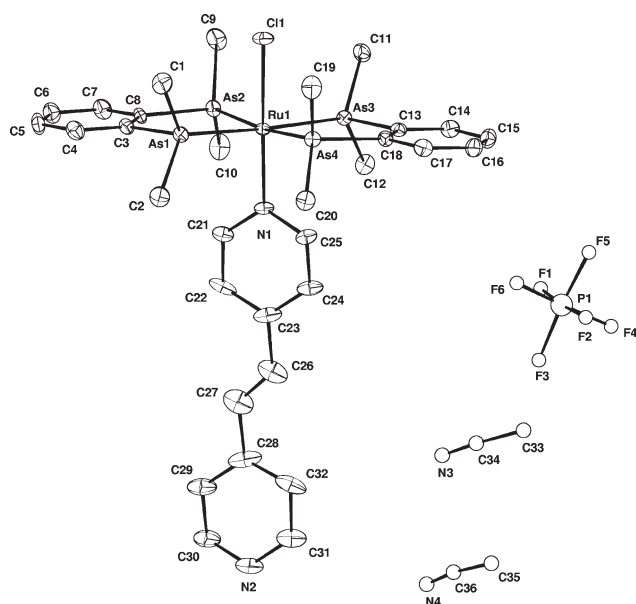


Fig. 2 Structural representation of the complex salt 4·2MeCN (50% probability ellipsoids).

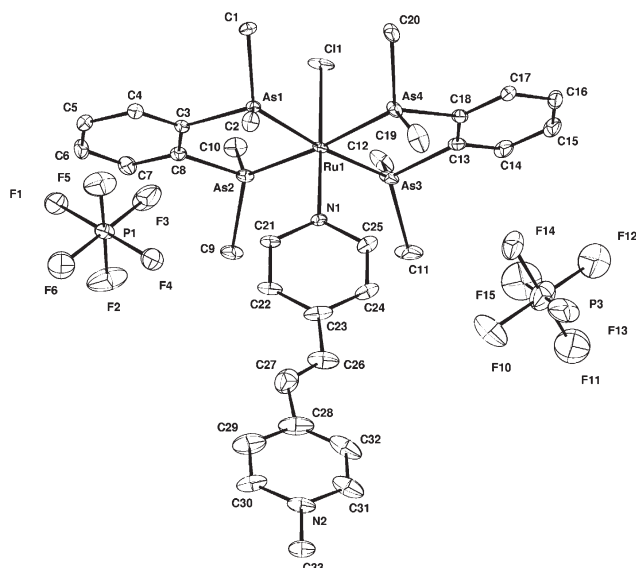


Fig. 3 Structural representation of the complex salt 7 (50% probability ellipsoids).

7 and 11 display relatively large quadratic NLO responses at the molecular level, these salts all adopt centrosymmetric crystal packing structures, so are not expected to show any bulk NLO effects. On the other hand, 1·2.5MeCN does crystallize non-centrosymmetrically, but the chromophore in this compound has a comparatively low β_0 value because the unmethylated pyrazine ligand is not an especially strong π -acceptor. However, we have previously reported the crystal structure of the acetone solvate of salt 13 which adopts the non-centrosymmetric orthorhombic space group $Pna2_1$.⁹ This material may therefore be worthy of further NLO studies, such as SHG screening or electro-optic measurements.

Comparisons with ruthenium(II) ammine complexes

We have found previously that the MLCT absorptions of complexes with electron-donating $trans$ - $\{Ru^{II}(Cl)(pdma)_2\}^+$ centres are found to high energy and have smaller molar extinction coefficients when compared with those of their Ru^{II} ammine analogues.⁹ We had therefore assumed that such arsine complexes will have considerably smaller molecular quadratic NLO responses than their ammine counterparts. The additional Stark spectroscopic data now available allow us to make direct quantitative comparisons to test this premise. Selected data for the two series of complex salts 6–9 and 12–14

Table 5 Selected interatomic distances (Å) and angles (°) for complex salts 1·2.5MeCN, 4·2MeCN, 7 and 11

	1·2.5MeCN	4·2MeCN	7	11
Ru1–N1	2.118(10)	2.114(4)	2.110(4)	2.081(5)
Ru1–As1	2.4270(15)	2.4133(7)	2.4127(11)	2.4094(7)
Ru1–As2	2.4290(15)	2.4228(7)	2.4210(12)	2.4163(7)
Ru1–As3	2.4320(15)	2.4122(7)	2.4226(12)	2.4210(7)
Ru1–As4	2.4259(15)	2.4179(7)	2.4179(12)	2.4159(7)
Ru1–Cl1	2.436(3)	2.4292(14)	2.441(3)	2.4360(16)
N1–Ru1–As1	94.0(3)	92.52(13)	92.27(16)	92.19(12)
N1–Ru1–As2	93.0(3)	93.82(12)	91.84(16)	91.63(13)
N1–Ru1–As3	93.9(3)	90.96(13)	94.67(16)	94.99(12)
N1–Ru1–As4	94.4(3)	92.70(12)	94.39(16)	94.43(13)
As1–Ru1–As2	172.98(6)	84.90(2)	85.51(4)	85.61(2)
As1–Ru1–As3	84.71(5)	176.46(3)	172.98(5)	172.72(3)
As1–Ru1–As4	94.65(5)	95.26(2)	93.16(4)	93.25(2)
As2–Ru1–As3	94.60(5)	94.17(2)	95.33(4)	95.39(3)
As2–Ru1–As4	85.03(5)	173.46(3)	173.67(5)	173.87(3)
As4–Ru1–As3	171.77(6)	85.27(2)	85.25(4)	84.99(2)
N1–Ru1–Cl1	178.6(3)	178.47(13)	179.11(18)	178.59(13)
As1–Ru1–Cl1	87.30(8)	88.01(4)	87.85(7)	87.62(4)
As2–Ru1–Cl1	85.69(8)	87.66(4)	87.29(8)	86.96(5)
As3–Ru1–Cl1	86.95(8)	88.54(4)	85.23(7)	85.23(4)
As4–Ru1–Cl1	84.83(8)	85.81(4)	86.48(8)	86.97(5)

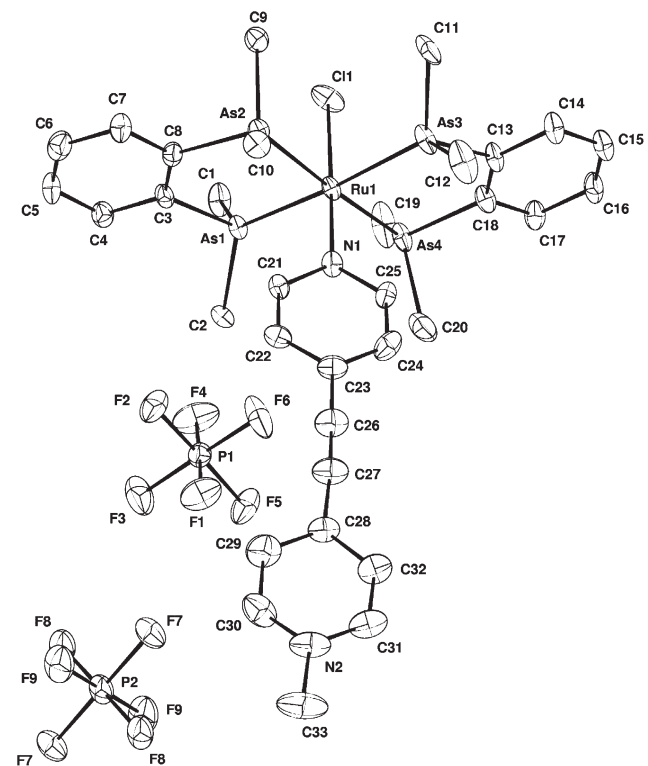


Fig. 4 Structural representation of the complex salt 11 (50% probability ellipsoids).

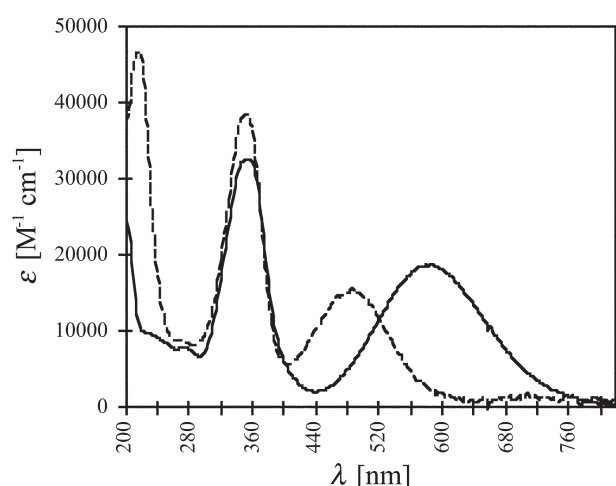
and for their $\{Ru^{II}(NH_3)_5\}^{2+}$ analogues^{5e,f,i} are presented in Table 6. Representative UV-VIS absorption spectra of the $n = 2$ complex salt 8 and of its $\{Ru^{II}(NH_3)_5\}^{2+}$ analogue 8A are shown in Fig. 5.

In every case, the MLCT bands of the arsine complexes are blue-shifted by *ca.* 0.6 eV when compared with those of their pentaammine analogues at 77 K. Previous comparative electrochemical studies have shown that this effect is largely attributable to a marked relative stabilisation of the Ru-based HOMOs in the arsine species.⁹ Although the molar extinction coefficients of the arsine complexes are *ca.* 40–50% lower than those of their pentaammine counterparts at room temperature,⁹ the f_{os} and μ_{12} values for the arsine chromophores are actually higher in each case at 77 K, because their band intensities increase substantially on freezing. For an example comparison, the room-temperature μ_{12} values for salts 8 and 8A are 5.5 and 6.8 D, respectively. It is noteworthy that the temperature

Table 6 MLCT absorption and Stark spectroscopic data for salts **6–9**, **12–14** and their $\{\text{Ru}^{\text{II}}(\text{NH}_3)_5\}^{2+}$ analogues.^a

Salt	$\lambda_{\text{max}}/\text{nm}$	E_{max}/eV	f_{os}	μ_{12}^b/D	$\Delta\mu_{12}^c/\text{D}$	$\Delta\mu_{\text{ab}}^d/\text{D}$	c_b^{2e}	$H_{\text{ab}}/\text{cm}^{-1f}$	$\beta_0^g/10^{-30}$ esu
6	491	2.53	0.41	6.6	14.3	19.4	0.13	6900	113
6A ^h	645	1.92	0.20	5.2	13.8	17.3	0.10	4700	120
7	515	2.41	0.33	6.0	16.9	20.7	0.09	5600	123
7A ^h	681	1.82	0.23	5.5	16.2	19.6	0.09	4100	175
8	506	2.45	0.94	10.0	20.6	28.7	0.14	6900	401
8A ⁱ	675	1.84	0.43	7.9	22.4	27.4	0.09	4300	482
9	501	2.48	1.04	10.5	22.2	30.6	0.14	6900	468
9A ⁱ	669	1.85	0.36	7.2	27.1	30.6	0.06	3500	475
12	516	2.40	0.37	6.4	17.4	21.6	0.10	5700	144
12A ^h	696	1.78	0.22	5.7	15.3	19.1	0.10	4300	186
13	525	2.36	0.41	6.7	17.9	22.4	0.10	5700	170
13A ^h	718	1.73	0.20	5.8	17.0	20.6	0.09	3900	229
14	536	2.31	0.46	7.3	17.9	23.1	0.11	5900	206
14A ^h	731	1.70	0.22	5.8	16.3	20.0	0.09	4000	225

^a Measured in butyronitrile glasses at 77 K. Analogous $\{\text{Ru}^{\text{II}}(\text{NH}_3)_5\}^{2+}$ complex salts denoted by **XA** (data for **15A** not available). ^b Calculated from eqn (2). ^c Calculated from $f_{\text{int}}\Delta\mu_{12}$ using $f_{\text{int}} = 1.33$. ^d Calculated from eqn (1). ^e Calculated from eqn (3). ^f Calculated from eqn (4). ^g Calculated from eqn (5). ^h Ref 5e. ⁱ Refs 5f,i.

**Fig. 5** UV/VIS absorption spectra of the salts **8** (dashed line) and **8A** (full line) at 298 K in acetonitrile.

dependence of μ_{12} is much more pronounced for the arsine salts than for the related ammine compounds.

The $\Delta\mu_{12}$ values show no consistent variation between the two types of complex, but are generally of similar magnitude (with the exception of those for **9** and **9A**). However, $\Delta\mu_{\text{ab}}$ and c_b^2 are generally a little larger and H_{ab} is somewhat larger for the arsine complexes. The values of β , calculated from eqn. (5), are slightly larger in each case for the ammine complexes; although the actual differences are within the experimental error, the observation of a consistent trend is reasonably convincing evidence that the chromophores with $\{\text{Ru}^{\text{II}}(\text{NH}_3)_5\}^{2+}$ electron donors have the larger NLO responses, albeit only marginally so. However, it should be borne in mind that this situation applies only in butyronitrile glasses at 77 K; the changes in the relative band intensities at room temperature imply that under such conditions the arsine complexes will have considerably smaller β values when compared with their pentaammine analogues, as originally anticipated.

Conclusion

MLCT absorption and electrochemical data clearly show that a *trans*- $\{\text{Ru}^{\text{II}}\text{Cl}(\text{pdma})_2\}^+$ centre is less electron-rich than a $\{\text{Ru}^{\text{II}}(\text{NH}_3)_5\}^{2+}$ unit. Analyses of Stark spectroscopic data according to the two-state model show that the β_0 responses of the arsine complexes are only a little smaller than those of the analogous $\{\text{Ru}^{\text{II}}(\text{NH}_3)_5\}^{2+}$ species in butyronitrile glasses at 77 K. However, this somewhat unexpected result can be traced to changes in the relative band intensities on freezing and is therefore not applicable to normal room temperature conditions where the β_0 values of the

pentaammine salts are expected to be considerably larger than those of their arsine counterparts. Nevertheless, the arsine complexes do show reasonably large molecular quadratic NLO responses, which are accompanied by considerable gains in visible transparency, thermal stability and also crystallising ability when compared with their pentaammine analogues. The electronic and optical properties of the arsine complexes show trends which mirror those observed previously in their ammine counterparts. In particular, the unusual linear optical behaviour of Ru^{II} ammine pyridyl polyene complexes is also found in the corresponding arsine species, but clear evidence for an accompanying decrease in β on chain extension is not observed. Further studies (such as long wavelength HRS and/or theoretical calculations) will be required to establish whether the behaviour of the arsine pyridyl polyene complexes is actually fundamentally different from that of the ammine species, and also to derive a greater understanding of the effects of temperature changes on the optical properties.

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