Ruthenium(II) ammine centres as efficient electron donor groups for quadratic non-linear optics

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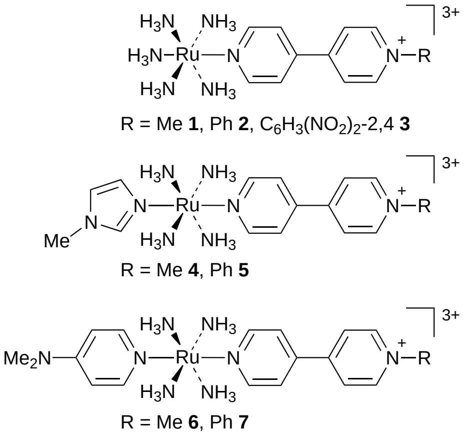
Ruthenium(II) complex salts *trans*-[Ru(NH$_3$)$_4$(L^D)(L^A)][PF$_6$]$_3$ (L^D = an N-donor ligand, L^A = a 4,4′-bipyridinium ligand) exhibit large, tunable static first hyperpolarizabilities β_0 which are associated with intense, visible metal-to-ligand charge-transfer excitations.

Organic materials possessing non-linear optical (NLO) properties are the focus of much current research activity directed towards applications in advanced electronics systems.[1] Within this field, transition-metal organometallic and coordination complexes have attracted limited attention,[2] but their great potential as novel NLO materials is yet to be fully explored.

Solution measurements of hyperpolarizability coefficients allow the correlation of NLO properties with molecular structure. This facilitates the rational design and synthesis of efficient NLO chromophores which may subsequently be incorporated into active materials. Extensive data concerning the first (quadratic) hyperpolarizability β is now available for purely organic compounds,[1] but corresponding information for metal complexes is scarce.[2] This situation is gradually being rectified and β values have been determined for selected complexes including bimetallic sesquifulvalenes,[3] Schiff-base derivatives,[4] and σ-acetylides.[5]

Recent reports show that ruthenium mixed-valence,[6] 2,2′-bipyridine (bipy),[7] and σ-acetylide[8] complexes can possess large β values, although two-photon excited luminescence may explain these results for the bipy complexes.[9] Ruthenium(II) ammine complexes are promising candidates as high β molecules due to the strong π-donor ability of the d^6 metal centres.[10] Such complexes are structurally versatile, and their readily accessible Ru$^{III/II}$ redox couples may permit reversible, molecular-level modulation of NLO properties.

A series of complex salts *trans*-[Ru^{II}(NH$_3$)$_4$(L^D)(L^A)][PF$_6$]$_3$ [Fig. 1; L^D = NH$_3$, L^A = *N*-methyl-4,4′-bipyridinium (MeQ$^+$) **1**, *N*-phenyl-4,4′-bipyridinium (PhQ$^+$) **2** or *N*-(2,4-dinitrophenyl)-4,4′-bipyridinium (DNPhQ$^+$) **3**; L^D = 1-methylimidazole (mim), L^A = MeQ$^+$ **4** or PhQ$^+$ **5**; L^D = 4-dimethylaminopyridine (dmap), L^A = MeQ$^+$ **6** or PhQ$^+$ **7**] have been synthesized by using established coordination chemistry based on [Ru^{II}(NH$_3$)$_5$(H$_2$O)][PF$_6$]$_2$ or *trans*-[Ru^{II}Cl(NH$_3$)$_4$(SO$_2$)]Cl;[11,12] **1**, **4** and **6** are known,[11,13] but the other salts are new. [PhQ$^+$]Cl and [DNPhQ$^+$]Cl were synthesized by using a modification of a literature report for *N*,*N*′-diphenyl-4,4′-bipyridinium dichloride.[14] All of the compounds have been fully characterized by using various techniques including UV–VIS spectroscopy and cyclic voltammetry,† and the first molecular hyperpolarizabilities β of the complex salts have been determined *via* the hyper-Rayleigh scattering (HRS) technique.[15]



R = Me **1**, Ph **2**, C$_6$H$_3$(NO$_2$)$_2$-2,4 **3**

R = Me **4**, Ph **5**

R = Me **6**, Ph **7**

Fig. 1 Structures of the complex cations in **1**–**7**

A common spectroscopic feature of low-valent ruthenium complexes of π-acceptor ligands are low-energy metal-to-ligand charge-transfer (MLCT) absorptions, the energies of which are governed by the electron-donor ability of the ruthenium centre and the ligand electron-acceptor capacity.[16] The exploitation of MLCT excited states as a basis for large β values has often been suggested,[2] but only very recently demonstrated.[8] The MeQ$^+$ ligand is a particularly effective π acceptor due to conjugation between the pyridyl rings.[17]

The complex salts show intense, broad d$_\pi$(Ru^{II}) → π*(L^A) MLCT bands in the visible region (Table 1). For a given L^D, the MLCT energies decrease in the order L^A = MeQ$^+$ > PhQ$^+$ > DNPhQ$^+$, with a red-shift of 70 nm going from **1** to **3**. This is because the electron acceptor strength of the ligand increases as the conjugation pathlength is extended. In keeping with this, the potentials for ligand-based reduction obtained *via* cyclic voltammetry (Table 1) show that the lowest unoccupied molecular orbital energy of PhQ$^+$ is lower than that of MeQ$^+$ by 140–160 mV. With L^A fixed, the MLCT energies decrease in the order L^D = NH$_3$ > mim > dmap, with a red-shift of 30 nm going from **2** to **7** reflecting the increasing basicity of L^D. The reversible Ru$^{III/II}$ oxidation waves are at constant potential, showing that the energy of the metal-based highest occupied molecular orbital is unaffected by the ligand changes. The MLCT bands are highly solvatochromic, with the maximum for **6** occurring at 604 nm in MeNO$_2$ and at 706 nm in HMPA. Such behaviour, which often accompanies large β values in organic compounds,[18] confirms that the MLCT excitations are the primary contributors to β in these complexes.

The HRS setup and the method for derivation of β were as described in a recent report.[19] All samples were passed through a 0.45 mm filter, and were checked for fluorescence which can interfere with the HRS signal.[9,20] The β values obtained are extremely large (Table 1), and similar to those reported for ruthenium organometallics.[8] A much smaller HRS β_{1064} value of 78 × 10^{-30} esu was found for the mixed-valence salt **8** (Fig. 2) in which the {Ru^{III}(NH$_3$)$_5$}$^{3+}$ centre acts as an electron acceptor.[9] Since salts **1**–**7** absorb in the region of the second harmonic at 532 nm (Table 1), their β values are resonantly

Table 1 Electrochemical, UV–VIS and non-linear optical data in acetonitrile for the salts *trans*-$[Ru(NH_3)_4(L^D)(L^A)][PF_6]_3$

			$E_{1/2}[Ru^{III/II}]$ (ΔE_p)/$E_{1/2}[L^{A+/0}]$ (ΔE_p)		λ_{max}[MLCT]/nm (ε/nm dm^3 mol^{-1} cm^{-1})	ε_{532}[b]	β_{1064}	β_0
Salt	L^D	L^A	*V vs.* SCE/mV[a]			(%)	10^{-30} esu	
1	NH_3	MeQ^+	0.46 (75)	−0.91 (65)	590 (15 800)	61	750	123
2	NH_3	PhQ^+	0.46 (75)	−0.75 (70)	628 (19 300)	32	858	220
3	NH_3	$DNPhQ^+$	0.46[d]	−0.40[e]	660 (16 900)	23	871	289
4[f]	mim	MeQ^+	0.47 (75)	−0.88 (70)	602 (16 200)	55	523	100
5	mim	PhQ^+	0.46 (70)	−0.73 (70)	648 (21 500)	31	874	266
6[f]	dmap	MeQ^+	0.46 (70)	−0.87 (65)	614 (17 200)	47	587	130
7	dmap	PhQ^+	0.46 (75)	−0.73 (65)	658 (20 000)	28	794	260

[a] Measured in solution 0.1 M in $[NBu^n_4]PF_6$ at a Pt bead working electrode with a scan rate of 200 mV s^{-1} (ferrocene internal reference $E_{1/2}$ = 0.40 V, ΔE_p = 65 mV). [b] Extinction at 532 nm as a percentage of that at the MLCT maximum. [c] β_{1064} is the uncorrected first hyperpolarizability measured by using a 1064 nm Nd : YAG laser fundamental; β_0 is the static hyperpolarizability estimated by using the two-level model.[22] A relative error of ±15% is estimated for β values. The quoted cgs units (esu) are converted into SI units (C^3 m^3 J^{-2}) by dividing by a factor of 2.693 × 10^{20}. [d] E_{pa} for an irreversible oxidation process. [e] E_{pc} for an irreversible reduction process. [f] Ref.13.

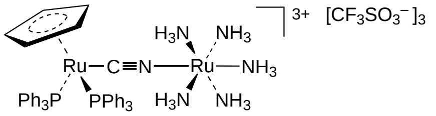


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Fig. 2 Structure of the diruthenium salt **8**

enhanced, to the greatest extent for **1** and to the least extent for **3**. Correlations between β and the intramolecular charge-transfer (ICT) energy have been found for dipolar organics in which a single ICT absorption dominates β.[21] In similar fashion, β for these complexes clearly increases as the MLCT band shifts to lower energy. This trend is evident despite the concomitant decreasing extent of resonance enhancement.

Static first hyperpolarizabilities β_0, which provide an estimate of the intrinsic molecular hyperpolarizability with resonance effects removed, were obtained by application of the two-level model.[22] The β_0 values are very large and are in excess of those for most NLO-active molecules. By way of contrast, the organic dye Brilliant Green has an ICT maximum at 632 nm and a β_0 value of 97 × 10^{-30} esu derived from HRS in 5% MeOH–1,4-dioxane at 1064 nm.[23] A broad inverse correlation between β_0 and the MLCT energy is observed for **1**–**7**.

In conclusion, we have demonstrated that readily synthesized and structurally versatile ruthenium coordination complexes can exhibit very large β and β_0 values which are associated with low-energy MLCT excitations. The MLCT energy is readily tuned by ligand modifications, which will allow the maximization of β_0 and the establishment of further structure–property correlations for this novel class of NLO molecules.

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Footnotes and References

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† The identity and purity of all of the ligands and complex salts were established by proton NMR spectroscopy and satisfactory elemental analyses.

1 *Nonlinear Optical Properties of Organic Molecules and Crystals*, ed. D. S. Chemla and J. Zyss, Academic Press, Orlando, 1987, vol. 1 and 2; *Molecular Nonlinear Optics*, ed. J. Zyss, Academic Press, New York, 1994.

2 S. R. Marder, in *Inorganic Materials*, ed. D. W. Bruce and D. O'Hare, Wiley, Chichester, 1992; N. J. Long, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 21.

3 U. Behrens, H. Brussaard, U. Hagenau, J. Heck, E. Hendrickx, J. Körnich, J. G. M. van der Linden, A. Persoons, A. L. Spek, N. Veldman, B. Voss and H. Wong, *Chem. Eur. J.*, 1996, **2**, 98.

4 P. G. Lacroix, S. Di Bella and I. Ledoux, *Chem. Mater.*, 1996, **8**, 541.

5 P. Nguyen, G. Lesley, T. B. Marder, I. Ledoux and J. Zyss, *Chem. Mater.*, 1997, **9**, 406.

6 W. M. Laidlaw, R. G. Denning, T. Verbiest, E. Chauchard and A. Persoons, *Proc. SPIE, Int. Soc. Opt. Eng.*, 1994, **2143**, 14.

7 C. Dhenaut, I. Ledoux, I. D. W. Samuel, J. Zyss, M. Bourgault and H. Le Bozec, *Nature*, 1995, **374**, 339.

8 I. R. Whittall, M. G. Humphrey, A. Persoons and S. Houbrechts, *Organometallics*, 1966, **15**, 1935; S. Houbrechts, K. Clays, A. Persoons, V. Cadierno, M. P. Gamasa and J. Gimeno, *Organometallics*, 1996, **15**, 5266.

9 I. D. Morrison, R. G. Denning, W. M. Laidlaw and M. A. Stammers, *Rev. Sci. Instrum.*, 1996, **67**, 1445.

10 Y. K. Shin, B. S. Brunschwig, C. Creutz and N. Sutin, *J. Phys. Chem.*, 1996, **100**, 8157 and references therein.

11 J. C. Curtis, B. P. Sullivan and T. J. Meyer, *Inorg. Chem.*, 1983, **22**, 224.

12 E. Tfouni and P. C. Ford, *Inorg. Chem.*, 1980, **19**, 72.

13 B. J. Coe, M. C. Chamberlain, J. P. Essex-Lopresti, S. Gaines, J. C. Jeffery, S. Houbrechts and A. Persoons, *Inorg. Chem.*, 1997, in the press.

14 B. Emmert and N. Roh, *Ber.*, 1925, **58**, 503.

15 K. Clays and A. Persoons, *Phys. Rev. Lett.*, 1991, **66**, 2980; K. Clays and A. Persoons, *Rev. Sci. Instrum.*, 1992, **63**, 3285.

16 P. Ford, De F. P. Rudd, R. Gaunder and H. Taube, *J. Am. Chem. Soc.*, 1968, **90**, 1187; C. R. Johnson and R. E. Shepherd, *Inorg. Chem.*, 1983, **22**, 2439.

17 P. Chen, M. Curry and T. J. Meyer, *Inorg. Chem.*, 1989, **28**, 2271.

18 M. S. Paley and J. M. Harris, *J. Org. Chem.*, 1991, **56**, 568.

19 S. Houbrechts, K. Clays, A. Persoons, Z. Pikramenou and J.-M. Lehn, *Chem. Phys. Lett.*, 1996, **258**, 485.

20 E. Hendrickx, C. Dehu, K. Clays, J. L. Brédas and A. Persoons, *ACS Symp. Ser.*, 1995, **601**, 82; M. C. Flipse, R. de Jonge, R. H. Woudenberg, A. W. Marsman, C. A. van Walree and L. W. Jenneskens, *Chem. Phys. Lett.*, 1995, **245**, 297.

21 L.-T. Cheng, W. Tam, G. R. Meredith, G. Rikken and E. Meijer, *Proc. SPIE, Int. Soc. Opt. Eng.*, 1989, **1147**, 61; A. E. Stiegman, E. Graham, K. J. Perry, L. R. Khundkar, L.-T. Cheng and J. W. Perry, *J. Am. Chem. Soc.*, 1991, **113**, 7658.

22 J. L. Oudar and D. S. Chemla, *J. Chem. Phys.*, 1977, **66**, 2664; J. L. Oudar, *J. Chem. Phys.*, 1977, **67**, 446; J. Zyss and J. L. Oudar, *Phys. Rev. A*, 1982, **26**, 2016.

23 P. Kaatz and D. P. Shelton, *J. Chem. Phys.*, 1996, **105**, 3918.

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