A cyclometallated ruthenium(ii) complex with a sterically hindered ligand displaying a long-lived MLCT excited state

Jean-Paul Collin,[a] Robert Kayhanian,[a] Jean-Pierre Sauvage,[a]* Giuseppe Calogero,[b] Francesco Barigelletti,[b] André De Cian[c] and Jean Fischer[c]

[a] *Laboratoire de Chimie Organo-Minérale, UA 422 au CNRS, Institut de Chimie, Université Louis Pasteur, 4 rue Blaise Pascal, F-67070 Strasbourg, France*
[b] *Istituto FRAE-CNR, via P. Gobetti 101, 40129 Bologna, Italy*
[c] *Laboratoire de Cristallochimie et de Chimie Structurale, UA 424 au CNRS, Institut de Chimie, Université Louis Pasteur, 4 rue Blaise Pascal, F-67070 Strasbourg, France*

Two cyclometallated ruthenium(II) complexes incorporating mono- or di-substituted phenanthroline moieties are synthesized and characterized by single-crystal X-ray diffraction; the complex with a sterically hindered ligand displays a long-lived MLCT excited state.

Transition-metal complexes exhibiting luminescence from metal-to-ligand charge transfer (MLCT) excited states have been the subject of numerous studies.[1] In this field, the d^6 polypyridyl complexes of Ru^{II},[2] Os^{II}[3,4] and Re^{I}[5] form the major class of such compounds. Recently, cyclometallated complexes[6,7] of d^6 and d^8 transition-metal ions have also shown interesting photophysical properties. Since ruthenium terpyridine type complexes are particularly suitable to build up multicomponent systems,[8] the search for compounds of this type displaying long-lived MLCT excited states at room temperature remains a stimulating challenge. Here, we describe the synthesis, crystal structures and photophysical properties of two luminescent cyclometallated ruthenium complexes. Interestingly, the photophysical properties of the compounds can be strongly modified by introducing small structural changes in the cyclometallating ligand.

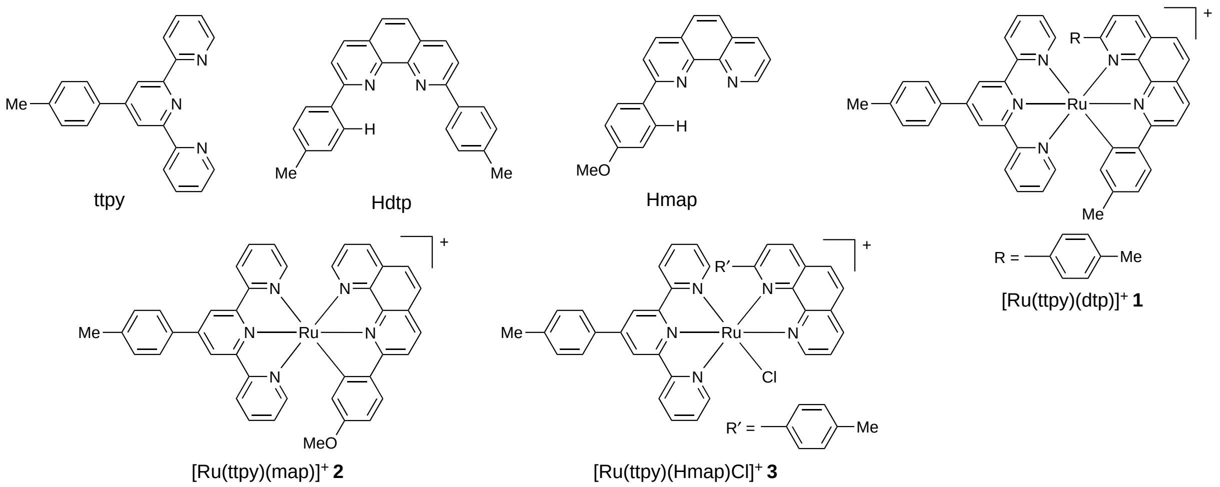
In the presently reported complexes, 4′-tolyl-2,2′:6′,6″-terpyridine (ttpy) affords NNN coordination. It is associated with the 1,10-phenanthroline ligand bearing different aromatic substituents in the 2 and 9 positions and leading to NNC coordination. The aromatic sustituents are two tolyl groups for Hdtp[9] and a *p*-anisyl group for Hmap[10] (Scheme 1).

The deep purple complexes $[Ru(ttpy)(dtp)]^+$ **1** and $[Ru(ttpy)(map)]^+$ **2** were prepared by the reaction of $[Ru(ttpy)Cl_3]$ with the phenanthroline ligand Hdtp or Hmap in refluxing acetic acid in the presence of one drop of *N*-ethylmorpholine. Considering that both cyclometallated (NNC) and the non-cyclometallated (NN) products could be obtained with Hmap, it is not surprising, in view of previous results[11] that Hdtp leads exclusively to the formation of the cyclometallated (NNC) compound. Satisfactory analytical data have been obtained for these complexes. Single crystals of **1** and **2** were obtained by slow diffusion of benzene into an acetonitrile solution of each compound. The structures of **1** and **2** were determined by single-crystal X-ray diffraction† and the ORTEP diagrams are shown in Fig. 1 and 2.

By comparing the X-ray structures of **1** and **2**, it is clear that the ruthenium(ii) coordination polyhedra are very similar, except for one particular Ru–N distance. In fact, the bond between the metal and the nitrogen atom *ortho* to the linkage point of the tolyl group borne by the phenanthroline nucleus is *ca.* 0.06 Å longer in **1** than in the unsubstituted compound **2**. This difference probably reflects the steric effect of the aromatic group in the vicinity of the Ru coordination sphere, which is also in agreement with the close proximity between the tolyl group and the central pyridine ring of the ttpy chelate. This stacking situation is likely to result in donor–acceptor interactions involving the tolyl group (donor) and the Ru-bonded central pyridine (acceptor). This would explain the very different photophysical behaviour of **1** as compared to **2**.

The electrochemical and spectroscopic data for **1** and **2** are collected in Table 1.

It is of note that whereas **2** is practically not luminescent in acetonitrile at room temperature, **1** luminesces and displays a



Scheme 1

relatively long-lived excited state (τ = 95 ns). In fact, **1** seems to be one of the longest-lived[12] terpy-type ruthenium(ii) complexes.

Clearly, the electronic properties of both compounds **1** and **2** seem to be almost identical (Table 1). The remarkable effect of the tolyl group onto the MLCT excited state lifetime of **1** could be related to the steric protection of the metal and strong rigidifying of the molecular edifice *via* π–π interaction with the ttpy ligand of the complex.

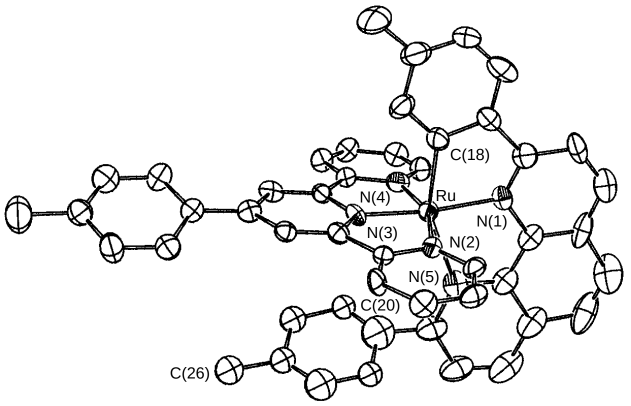


Fig. 1 ORTEP view of the cationic part of **1** with partial labelling scheme. Ellipsoïds are scaled to enclose 30% of the electronic density. One orientation of the C(20)–C(26) tolyl moiety is shown. Hydrogen atoms are omitted. Selected distances (Å) and angles (°): Ru–N(1) 2.010(2), Ru–N(2) 2.256(3), Ru–N(3) 2.031(3), Ru–N(4) 1.942(3), Ru–N(5) 2.052(2), Ru–C(18) 2.037(4); N(1)–Ru–N(2) 76.6(1), N(1)–Ru–C(18) 78.3(1), N(1)–Ru–N(2) 100.6(1), N(3)–Ru–N(4) 79.8(1), N(4)–Ru–C(18) 93.5(1), N(2)–Ru–N(4) 111.5(1).

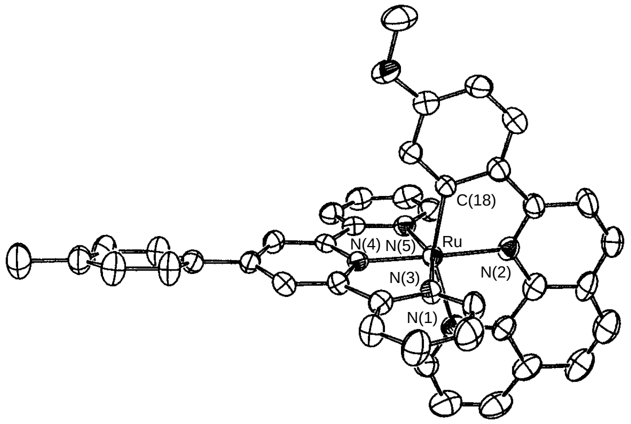


Fig. 2 ORTEP view of the cationic part of **2** with partial labelling scheme. Ellipsoïds are scaled to enclose 30% of the electronic density. Selected distances (Å) and angles (°): Ru–N(1) 2.198(6), Ru–N(2) 2.009(6), Ru–C(18) 2.030(8), Ru–N(3) 2.050(5), Ru–N(4) 1.961(6), Ru–N(5) 2.062; N(1)–Ru–N(2) 76.9(2), N(1)–Ru–N(3) 93.7(2), N(1)–Ru–N(4) 105.4(2), N(2)–Ru–C(18) 79.1(3), N(3)–Ru–N(4) 78.8(2), N(4)–Ru–C(18) 98.6(3).

Table 1 Electrochemical[a] and spectroscopic data[b]

	Redox potential; V *vs.* SCE					
	$Ru^{3+/2+}$	$L^{0/1-}$	λ_{abs}/nm	λ_{em}/nm	τ/ns	Φ
1	0.54	−1.57	527	802	95	0.02
2	0.54	−1.54	518	[c]	[c]	[c]
3	0.77	−1.50	508	820	6.6	≤1 × 10^{-5}

[a] Cyclic voltammetry in MeCN solution (0.1 m $NBu^n_4BF_4$); Pt working electrode. [b] MeCN solutions; room temperature; uncorrected luminescence band maxima. Luminescence quantum yields and lifetimes were determined as in F. Barigelletti, L. Flamigni, M. Guardigli, A. Juris, M. Beley, S. Chodorowski-Kimmes, J.-P. Collin and J.-P. Sauvage, *Inorg. Chem.*, 1996, **35**, 136. [c] Too weak to detect.

This work has been supported by the CNRS (France) and by CNR (Italy). We thank Patrice Staub for his technical assistance.

Footnotes

* E-mail: sauvage@chimie.u-strasbg.fr

† *Crystal data*: **1**, purple crystals from benzene–acetonitrile. $2(C_{48}H_{36}F_6N_5PRu)\cdot CH_3CN$, M = 1898.8, monoclinic, space group $P2_1/n$; a = 21.196(6), b = 17.212(5), c = 11.312(3) Å, β = 95.40(2), U = 4103(3) Å^3, Z = 2, D_c = 1.537 g cm^{-3}, μ = 41.337 cm^{-1}. Measurements: Philips PW1100/16, θ–2θ flying step-scans, Cu-Kα graphite-monochromated radiation (λ = 1.5418 Å), T = 173 K. 5396 reflections (θ = 3–54°), of which 4334 unique with $I > 3\sigma(I)$ were used for structure solution (direct methods) and refinement (full-matrix least squares); R = 0.081, R_w = 0.143. The C(20)–C(26) tolyl moiety adopts two orientations (50/50); for one of them a MeCN solvent molecule is present. Atoms C(25)–C(26) in both orientations were introduced as fixed contributors with isotropic temperature factors allowed to vary during refinement. All other non-hydrogen atoms were refined anisotropically. The hydrogen atoms were calculated and fixed in idealized positions [d(C–H) = 0.95 Å, B(H) = 1.3 B_{equiv} for the carbon to which it was attached] with the exception of C(20)–C(26) tolyl and CH_3CN protons not introduced. **2**, dark blue crystals from benzene–acetonitrile. $C_{41}H_{30}F_6N_5OPRu$, M = 854.8; monoclinic, space group $P2_1/n$; a = 12.535(3), b = 16.512(4), c = 18.334(5) Å, β = 107.86(2), U = 3611(3) Å^3, Z = 4, D_c = 1.572 g cm^{-3}, μ = 5.387 cm^{-1}. Measurements: Nonius MACH3, θ–2θ scans, Mo-Kα graphite-monochromated radiation (λ = 0.7107 Å), T = 283 K. 8376 reflections (θ = 2–26°), of which 3664 unique with $I > 3\sigma(I)$ were used for structure solution (direct methods) and refinement (full-matrix least squares); R = 0.056, R_w = 0.076. The fluorine atoms of the PF_6^- anion are disordered over two positions (50/50) and where assigned isotropic temperature factors. All other non-hydrogen atoms were refined anisotropically and treated as above. For all computations, the Nonius MolEN/Vax package was used.[13]

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/389.

References

1 V. Balzani and F. Scandola, *Supramolecular Photochemistry*, Ellis Horwood, Chichester, 1991.
2 A. Juris, V. Balzani, F. Barigelletti, S. Campagna, P. Belser and A. Von Zelewsky, *Coord. Chem. Rev.*, 1988, **84**, 85.
3 C. Creutz, M. Chou, T. L. Netzel, M. Okamura and N. Sutin, *J. Am. Chem. Soc.*, 1980, **102**, 1309.
4 E. M. Kober, J. L. Marshall, W. J. Dressick, B. P. Sullivan, J. V. Caspar and T. J. Meyer, *Inorg. Chem.*, 1985, **24**, 2755.
5 A. J. Lees, *Chem. Rev.*, 1987, **87**, 711.
6 F. Barigelletti, D. Sandrini, M. Maestri, V. Balzani, A. Von Zelewsky, L. Chassot, P. Jolliot and U. Maeder, *Inorg. Chem.*, 1988, **27**, 3644; J. P. Collin, M. Beley and J. P. Sauvage, *Inorg. Chim. Acta*, 1991, **186**, 91.
7 P. Spellane and R. J. Watts, *Inorg. Chem.*, 1993, **32**, 5633.
8 J.-P. Sauvage, J.-P. Collin, J.-C. Chambron, S. Guillerez, C. Coudret, V. Balzani, F. Barigelletti, L. De Cola and L. Flamigni, *Chem. Rev.*, 1994, **94**, 993.
9 C. O. Dietrich-Buchecker, J. F. Nierengarten, J. P. Sauvage, N. Armaroli, V. Balzani and L. De Cola, *J. Am. Chem. Soc.*, 1993, **115**, 11 237.
10 S. Chardon-Noblat and J.-P. Sauvage, *Tetrahedron*, 1991, **47**, 5123.
11 E. C. Constable and M. J. Hannon, *Inorg. Chim. Acta*, 1993, **211**, 101.
12 M. Maestri, N. Armaroli, V. Balzani, E. C. Constable and A. M. W. Cargill Thompson, *Inorg. Chem.*, 1995, **34**, 2759.
13 C. K. Fair, in MolEN, *An Interactive Intelligent System for Crystal Structure Analysis*, Nonius, Delft, The Netherlands, 1990.

Received in Basel, Switzerland, 4th December 1996; Com. 6/08175D