

A mixed-bridging ligand nonanuclear Ru(II) dendrimer containing a tris-chelating core. Synthesis and redox properties†

Julien Leveque,^a Cécile Moucheron,^a Andrée Kirsch-De Mesmaeker,^a Frédérique Loiseau,^b Scolastica Serroni,^b Fausto Puntoriero,^b Sebastiano Campagna,^b Hélène Nierengarten^c and Alain Van Dorselaer^c

^a Université Libre de Bruxelles, Laboratory of Organic Chemistry and Photochemistry, CP 160/08, 50 av. F.D. Roosevelt, 1050 Bruxelles, Belgium. E-mail: akirsch@ulb.ac.be; Tel: 32 2 6503017

^b Department of Inorganic, Analytical & Physical Chemistry, University of Messina, Via Sperone 31, I-98166 Messina, Italy. E-mail: photochem@chem.unime.it; Tel: 39 090 6765737

^c UMR 7509, LSMBO-ECPM, 25 rue Becquerel, 67087 Strasbourg, France. E-mail: vandors@chimie.u-strasbg.fr; Tel: 33 3 88416887

Received (in Cambridge, UK) 9th January 2004, Accepted 23rd January 2004

First published as an Advance Article on the web 4th March 2004

The first ligand-cored dendrimer based on branching Ru(II) centers and containing mixed polypyridine bridging ligands has been prepared; redox experiments suggest that the redox-active core is not reduced at the expected potential, probably as a consequence of shielding induced by the rigid dendritic array.

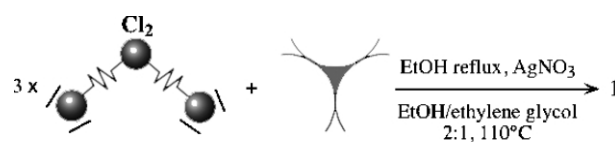
Metallo-dendrimers are at the center of an increasing interest for both fundamental reasons and potential applications.¹ In particular, metallo-dendrimers made of Ru(II) building blocks have allowed information to be gained on the electronic interactions occurring within supramolecular dendritic structures and investigations on multi-electron redox processes and photoinduced energy migration. The main goal within this specific field is the search for light-harvesting antenna units or artificial photosynthesis and multi-electron storage systems.² The metallo-dendrimers in which the metal centers behave both as photo- and redox-active subunits and as branching centres are particularly attractive. They allow indeed the accumulation of a large number of metal subunits in a minimum space. Systems like these containing 2,3-bis(2'-pyridyl)pyrazine (2,3-dpp),³ 1,4,5,8,9,12-hexaazatriphenylene (HAT),⁴ bis-benzimidazolone subunits,⁵ and tetrapyrido[3,2-a:2',3'-c:3'',2''-h:2''',3'''-j]phenazine⁶ as bridging ligands have been probably the most investigated until now. All these species share two common features: (i) they are normally based on a metal center as the core; (ii) they contain only one type of bridging ligand. Ru(II) dendrimers constructed with two bridging ligands are indeed extremely rare.⁷ Moreover, a few examples of Ru(II) dendrimers built on a purely organic core have been reported,⁸ and in this latter case the core has only a structural function and is not an essential part of the chromophore/redox subunit(s).⁹

In this work we report the synthesis of a nonanuclear Ru(II) dendrimer, [μ -HAT{Ru(μ -2,3-dpp)Ru(bpy)₂}]₃¹⁸⁺ (**1**, see Fig. 1), containing two different bridging ligands, namely 2,3-dpp and HAT. The tris-chelating HAT ligand also plays the role of the dendrimer core, and has both a structural and a functional role. To

our knowledge, **1** is the first compound based on a tris-chelating ligand exhibiting these features. The redox behaviour, including some unusual properties, is also presented.

Design and synthesis are based on the “complexes as ligands/complexes as metals” strategy,¹⁰ which is illustrated in Scheme 1. The tris-chelating bridging ligand HAT was reacted with three equivalents of the mono-functional “complex-metal” [Cl₂Ru(μ -2,3-dpp)Ru(bpy)₂]₂⁴⁺ species (**2**). As a first step, **2** was refluxed for 2 h in EtOH containing AgNO₃ in order to substitute the chlorides by solvent molecules. The HAT ligand was then added and the reaction was carried out in EtOH/ethylene glycol (2:1 v/v) at 110 °C for 16 h. After elimination of the AgCl precipitate by centrifugation, the product was precipitated with NH₄PF₆ and finally separated by extractions with ethanol.

The electrospray mass spectrum (Fig. 2 and Table 1) indicates that **1** is the only product of the reaction, however the peak at 537.4 (rel. int.: 15%) suggests the presence of an impurity due to unreacted **2** (ESMS, see ESI[†]) or decomposition of **1**.¹¹ Interestingly, counter ion exchange proved to be incomplete (Table 1, presence of Cl⁻ and PF₆⁻): this confirms that counterions are tightly bound to the positively charged complex in this type of



Scheme 1 Synthetic procedure.

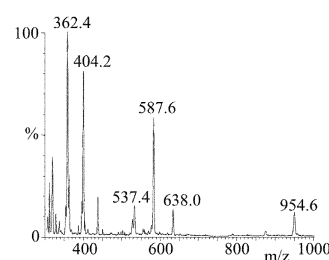


Fig. 2 ESMS spectrum of **1**.

Table 1 ESMS spectrum data of **1**. M¹⁸⁺ = 4423.6

<i>m/z</i> exp	Attribution	<i>m/z</i> calc	Rel. Int.
954.6	M ¹⁸⁺ + 8PF ₆ ⁻ + 4Cl ⁻	954.2	12%
638.0	M ¹⁸⁺ + 3PF ₆ ⁻ + 7Cl ⁻	638.3	12%
587.6	M ¹⁸⁺ + 5PF ₆ ⁻ + 4Cl ⁻	587.8	58%
442.0	M ¹⁸⁺ + 6PF ₆ ⁻	441.1	20%
404.2	M ¹⁸⁺ + 2PF ₆ ⁻ + 4Cl ⁻	404.6	82%
362.4	M ¹⁸⁺ + PF ₆ ⁻ + 4Cl ⁻	362.3	100%
323.5	M ¹⁸⁺ + 3PF ₆ ⁻	323.9	39%

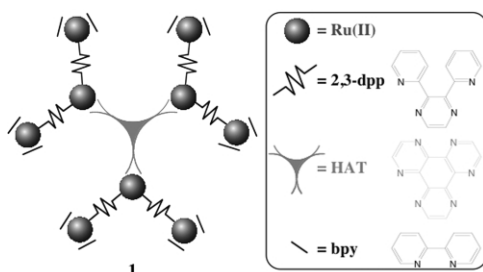


Fig. 1 Schematic representation of **1**.

† Electronic supplementary information (ESI) available: ESMS relevant data with attribution of **2**, detailed synthesis of **1** and conditions of the redox experiments. See <http://www.rsc.org/suppdata/cc/b4/b400311j/>

highly-charged dendrimers,¹² and are difficult to be exchanged.^{13,14}

The redox behaviour of **1** was investigated in deaerated acetonitrile solution (see details in ESI†) and the relevant data are gathered in Table 2, together with those of the related species **2**, [μ -HAT{Ru(bpy)₂}₃]⁶⁺ (**3**),¹⁵ [Ru{(μ -2,3-dpp)Ru(bpy)₂}₃]⁸⁺ (**4**) and [Ru{(μ -2,3-dpp)Ru{(μ -2,3-dpp)Ru(bpy)₂}₂}]₃²⁰⁺ (**5**). Metal polypyridine complexes are known to exhibit metal-centered reversible oxidation processes and ligand-centered reversible reduction processes. Compound **1** contains nine metal centers, so in principle nine reversible oxidation processes are expected in the oxidation window investigated (<2.20 V vs SCE). Cyclic voltammetry indicated a single reversible oxidation process at +1.53 V; differential pulse voltammetry also revealed a second process at about +2.13 V. By comparison with the data of other related species (Table 2), the first process can be assigned to the simultaneous one-electron oxidation of the six peripheral (μ -2,3-dpp)Ru(bpy)₂²⁺ subunits. The second oxidation can be assigned to the inner (μ -2,3-dpp)₂Ru(μ -HAT)²⁺ subunits, however since it occurs at a potential close to the limit of the measurable oxidation window, it is not possible to state whether this process involves the three inner metal centers or only one of them.

The reduction behaviour is quite intriguing: from the data of the parent complexes (Table 2), a one-electron reduction process involving the three-times coordinated central HAT ligand is expected, most likely around -0.25 V/SCE or even at less negative potentials, followed by two processes, both probably trielectronic in nature, corresponding to the reductions of the 2,3-dpp bridges, in the range -0.50/-0.70 V. However, both cyclic voltammetry and differential pulse voltammetry revealed only the presence of two reversible processes, involving approximately the same number of electrons, at -0.56 and -0.68 V (Table 2). Such processes are assigned to the reduction of the 2,3-dpp bridging ligands. Apparently, HAT is not reduced at the expected potential. These results tend to suggest that, due to the structure of **1**, the core of the species cannot approach the electrode surface. This shielding is not a totally novel observed phenomenon in dendrimer electrochemistry. Indeed it has been already reported for large dendrimers containing Co-phthalocyanines,¹⁶ Zn-porphyrins¹⁷ and iron-sulfur clusters¹⁸ as cores. In contrast, it is the first time that it is reported for a dendrimer based on Ru(II) polypyridine building blocks. In other large Ru(II) and Os(II) dendrimers, the dendrimer dimension never affected core oxidation.^{3,19} It should be noted however that in the present case the process is a reduction, not an oxidation as in all the known examples. Therefore, the metal-containing branches could have a different effect on reduction, at the level of the connection between dendrimer core and electrode. On the other hand, the shielding or protection of the HAT core in the trinuclear [μ -HAT{Ru(bpy)₂}₃]⁶⁺ species adsorbed on colloidal silver has been inferred from Surface Enhanced Resonance Raman Spectroscopy (SERRS) results.²⁰ Finally, one point remains to be considered. Although HAT is not reduced at the expected potential, it should be reduced upon first reduction of the 2,3-dpp ligands. Actually, the first electron added to a 2,3-dpp ligand should rapidly be transferred to the LUMO of the central HAT belonging to the (μ -

2,3-dpp)₂Ru(μ -HAT)²⁺ subunit. Indeed this process can be regarded as an energetically favorable electron transfer or hopping between polypyridine ligands linked to the same metal ion and such a process is known to occur in picosecond timescale (or less) in Ru(II) polypyridine complexes.²¹ Therefore the first reduction of **1** could involve more than three electrons. As the determination of the number of electrons is difficult in this case since the two reduction processes are partially overlapped, we cannot confirm at this stage, the electron transfer hypothesis from one 2,3-dpp ligand to the central HAT ligand.

We thank ARC (Action de Recherche Concertée), program 2002–2003, MIUR, the EU-TMR program (no. ERBFMRX-CT98-0226) and COST D14 for financial support. JL also thanks FRIA (Fonds pour la Recherche dans l'Industrie et l'Agriculture, Belgium) for PhD fellowship.

Notes and references

- (a) G. R. Newkome, C. N. Moorefield and F. Vögtle, *Dendrimers and Dendrons*, VCH, Weinheim, 2001; (b) *C. R. Chimie*, 2003, **6**, issue 6–8, p. 709–1210. Thematic issue on *Dendrimers and Nanosciences*, ed. D. Astruc.
- S. Campagna, S. Serroni, F. Puntoriero, C. Di Pietro and V. Ricevuto, in *Electron Transfer in Chemistry*, Vol. 5, ed. V. Balzani, Wiley-VCH, Weinheim, 2001, p. 186.
- V. Balzani, S. Campagna, G. Denti, A. Juris, S. Serroni and M. Venturi, *Acc. Chem. Res.*, 1998, **31**, 26 and refs. therein.
- C. Moucheron, A. Kirsch-De Mesmaeker, A. Dupont-Gervais, E. Leize and A. Van Dorsselaer, *J. Am. Chem. Soc.*, 1996, **118**, 12834 and refs. therein.
- M.-A. Haga, M. M. Ali and R. Arakawa, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 76.
- F. M. MacDonnell, K.-J. Kim, K. L. Wouters and R. Konduri, *Coord. Chem. Rev.*, 2003, **242**, 47 and refs. therein.
- S. Serroni, S. Campagna, G. Denti, T. E. Keyes and J. G. Vos, *Inorg. Chem.*, 1996, **35**, 4513.
- For a few examples, see: (a) G. R. Newkome, E. He and L. A. Godinez, *Macromolecules*, 1998, **31**, 4382; (b) G. R. Storrie, K. Takada and H. Aburuña, *Langmuir*, 1999, **15**, 872.
- To our knowledge, two exceptions to this rule have been reported: (a) S. Campagna, G. Denti, S. Serroni, M. Ciano and V. Balzani, *Inorg. Chem.*, 1991, **30**, 3728; (b) ref. 6.
- S. Serroni, S. Campagna, F. Puntoriero, C. Di Pietro, F. Loiseau and N. D. McClenaghan, *Chem. Soc. Rev.*, 2001, **30**, 367.
- It cannot be excluded that the presence of **2** could originate from decomposition of **1** by ESMS. Indeed such processes had been observed with heteronuclear Ru-Rh trimetallic species with a central trischelating HAT: see P. Didier, L. Jacquet, A. Kirsch-De Mesmaeker, R. Hueber and A. Van Dorsselaer, *Inorg. Chem.*, 1992, **31**, 4803.
- (a) S. Campagna, A. Giannetto, S. Serroni, G. Denti, S. Trusso, F. Mallamace and N. Micali, *J. Am. Chem. Soc.*, 1995, **117**, 1754; (b) L. Latterini, G. Pourtois, C. Moucheron, R. Lazzaroni, J.-L. Brédas, A. Kirsch-De Mesmaeker and F. C. De Schryver, *Chem. Eur. J.*, 2000, **6**, 1331.
- For the electrochemical investigation, the sample has been several times reprecipitated with hexafluorophosphate salt, in order to obtain the complex preferentially under the form of the PF₆ salt.
- We have to mention that the preparation of **1** was not straightforward. Many trials were needed to identify the right conditions (see ESI†).
- (a) A. Masschelein, A. Kirsch-De Mesmaeker, C. Verhoeven and R. Nasielski-Hinkens, *Inorg. Chim. Acta*, 1987, **129**, L13; (b) L. Jacquet and A. Kirsch-De Mesmaeker, *J. Chem. Soc., Faraday Trans.*, 1992, **88**, 2471.
- M. Kimura, Y. Sugihara, T. Muto, K. Hanabusa, H. Shirai and N. Kobayashi, *Chem. Eur. J.*, 1999, **5**, 3495.
- K. W. Pollak, J. W. Leon, J. M. J. Fréchet, M. Maskus and H. D. Aburuña, *Chem. Mater.*, 1998, **10**, 30.
- C. B. Gorman, J. C. Smith, M. W. Hager, B. L. Parkurst, H. Sierzputowska and C. A. Haney, *J. Am. Chem. Soc.*, 1999, **121**, 9958.
- P. Ceroni, F. Paolucci, C. Paradisi, A. Juris, S. Roffia, S. Serroni, S. Campagna and A. J. Bard, *J. Am. Chem. Soc.*, 1998, **120**, 5480.
- F. Vanhecke, K. Heremans, A. Kirsch-De Mesmaeker, L. Jacquet and A. Masschelein, *J. Raman Spectrosc.*, 1989, **20**, 617.
- J. Andersson, F. Puntoriero, S. Serroni, A. Yartsev, T. Pascher, T. Polivka, S. Campagna and V. Sundström, *Faraday Discuss.*, in press.

Table 2 Redox data of **1** and related species in acetonitrile vs SCE. Only relevant data are given. Number of electrons exchanged given in brackets

	<i>E</i> (1/2) _{ox} , V	<i>E</i> (1/2) _{red} , V
2	+0.82 (1); +1.57(2)	-0.72(1); -0.88(1)
3	+1.61(1); +1.87(1); +2.12(1)	-0.25(1); -0.58(1)
4	+1.53(3)	-0.56(1); -0.63(1)
5	+1.53(6); +2.11(1); +2.44(3) ^a	
1	+1.53(6); +2.13 ^b	-0.56; -0.68 ^c

^a Second and third processes are recorded in liquid SO₂ (from ref. 19). ^b The number of electrons for this process has not been defined (see text). ^c Both reductions approximately involve 3 electrons each.