

## Synthesis and Characterization by Electrospray Mass Spectrometry of a Novel Dendritic Heptanuclear Complex of Ruthenium(II)

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The fascination for supramolecular edifices and for nanometer-sized molecules is extending continuously, especially as new synthetic strategies lead to novel materials with specific functions, such as information recording, conversion of light into chemical energy, and catalysis.<sup>1</sup> In this regard, dendrimers, also called arborols or “cascade molecules”, are of great interest.<sup>2</sup> More particularly, dendrimers incorporating metallic units are promising of potential new applications.<sup>3</sup> Polynuclear transition metal complexes of dendritic nature were first described by a team from Pisa, Messina, and Bologna.<sup>4</sup> These authors have developed a procedure to synthesize compounds of desired nuclearity and chemical structure by using metal complexes as building blocks,<sup>3f,5</sup> leading in some cases to a nuclearity as high as 22 metals in the dendrimer. Unfortunately, an unequivocal characterization of these complexes is still missing, mainly due to stereogenic problems. Indeed, because of the numerous diastereoisomers in polynuclear compounds composed of polyazaaromatic Ru(II) complexes, the characterization by NMR is of limited use, so that it relies on “sporting methods” which are often nonconclusive in the decision of formulation (e.g., infrared, resonance Raman, UV–visible absorption and emission spectroscopy, electrochemistry, etc.<sup>4,5a,6</sup>). Although these problems have not prevented the synthesis and study of multinuclear species, this limits severely the advancement of knowledge.

Electrospray mass spectrometry (ESMS) introduced by Fenn and co-workers<sup>7</sup> has been shown to be a powerful technique for analyzing multiply-charged ions, primarily applied to biomolecules.<sup>8</sup> Indeed, contrary to conventional MS methods

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(1) (a) Lehn, J. M. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1304–1319. (b) Whitesides, J. M.; Mathias, J. P.; Seto, C. T. *Science* **1991**, *254*, 1312–1319.

(2) (a) Newkome, G. R.; Moorefield, C. N.; Vögtle, F. *Dendritic Molecules*; Verlag Chemie: Weinheim, Germany, 1996. (b) Wooley, K. L.; Hawker, C. J.; Fréchet, J. M. J. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 82–85. (c) Gopidas, K. R.; Leheny, A. R.; Caminati, G.; Turro, N. J.; Tomalia, D. A. *J. Am. Chem. Soc.* **1991**, *113*, 7335–7342.

(3) (a) Haggin, J. *Chem. Eng. News* **1995** (Feb. 6), 26–27. (b) Balzani, V. *New Sci.* **1994** (Nov.), 31–34. (c) Knapen, J. W. J.; van der Made, A. W.; de Wilde, J. C.; van Leeuwen, P. W. N. M.; Wijkens, P.; Grove, D. M.; van Koten, G. *Nature* **1994**, *372*, 659–663. (d) Constable, E. C.; Harverson, P. J. *Chem. Soc., Chem. Commun.* **1996**, 33–34. (e) Dagan, R. *Chem. Eng. News* **1996** (July 8), 26–30. (f) Balzani, V.; Juris, A.; Venturi, M.; Campagna, S.; Serroni, S. *Chem. Rev.* **1996**, *96*, 759–833.

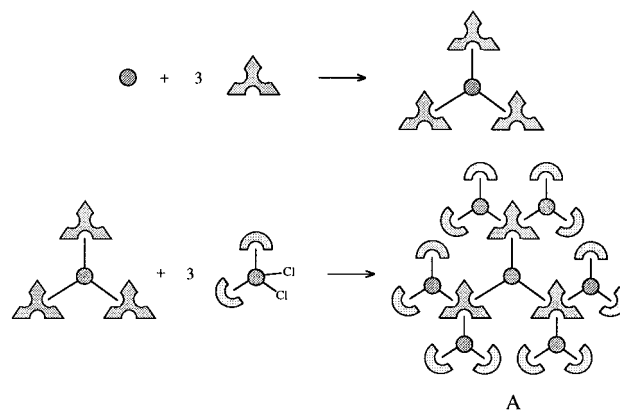
(4) Serroni, S.; Denti, G.; Campagna, S.; Juris, A.; Ciano, M.; Balzani, V. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1493–1495.


(5) (a) Denti, G.; Campagna, S.; Serroni, S.; Ciano, M.; Balzani, V. *J. Am. Chem. Soc.* **1992**, *114*, 2944–2950. (b) Campagna, S.; Denti, G.; Serroni, S.; Ciano, M.; Balzani, V. *Inorg. Chem.* **1991**, *30*, 3278.

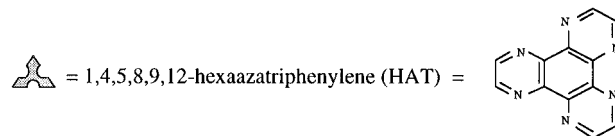
(6) Elemental analysis, which is also often given, is not a univocal proof for such nanostructures because of the unknown number of recrystallization molecules and nature of counterions (see further).

(7) (a) Yamashita, M.; Fenn, J. B. *J. Phys. Chem.* **1984**, *88*, 4451–4459. (b) Yamashita, M.; Fenn, J. B. *J. Phys. Chem.* **1984**, *88*, 4671–4675.

### Scheme 1



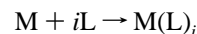
The ● represents ruthenium (II) atoms,  1,10-phenanthroline and



which show a lot of undesirable fragment ions in the mass spectra, the ESMS provides a quite simple mass pattern and allows the determination of molecular mass accurately with high sensitivity. Although this technique is not limited to biomolecules and has been applied to the identification of metal complexes,<sup>9</sup> no ESMS characterization of polynuclear polyazaaromatic complexes of type A (Scheme 1), with a total charge higher than 8+ has been examined in the literature up to now.<sup>10</sup> The aim of this work consists of removing these limitations and opening the way to future design of artificial nanostructures with nonambiguous characterizations. Thus a new dendritic heptametallic Ru(II) complex (A) and its unambiguous characterization by ESMS are reported. This treelike coordination complex is, to our knowledge, the highest charged transition metal complex ever characterized by ESMS.

Compound A is prepared from Wilkinson's complex and 1,4,5,8,9,12-hexaazatriphenylene (HAT) as a trischelating ligand, studied extensively in mono- and polymetallic complexes in the Belgian laboratory.<sup>11</sup>

The synthetic strategy is similar to that already described by Balzani and co-workers.<sup>4,5a</sup> It is based on the use of one complex as a metal M and of another complex as a ligand L in the reaction



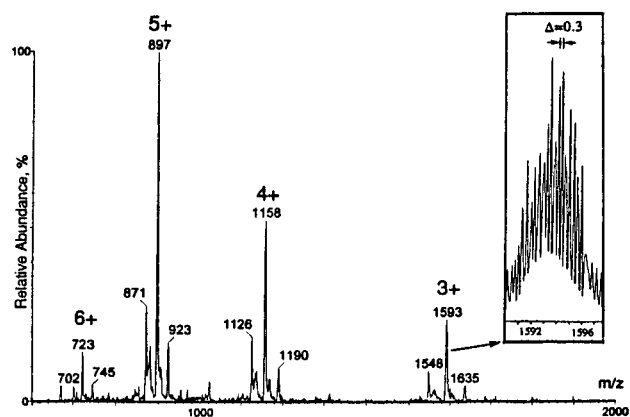
In the first step, Ru(HAT)<sub>3</sub>Cl<sub>2</sub> is prepared from Ru(DMSO)<sub>4</sub>Cl<sub>2</sub> and three HAT ligands. This central core contains six new chelating sites to which six units can be grafted to yield the heptametallic complex (Scheme 1).

(8) (a) Fenn, J. B.; Mann, M.; Meng, C. K.; Wong, S. K.; Whitehouse, C. *Science* **1989**, *246*, 64–71. (b) Fenn, J. B.; Mann, M.; Meng, C. K.; Wong, S. K. *Mass. Spectrom. Rev.* **1990**, *9*, 37.

(9) (a) Katta, V.; Chowdhury, S. K.; Chait, B. T. *J. Am. Chem. Soc.* **1990**, *112*, 5348–5349. (b) Colton, R.; James, B. D.; Potter, I. D.; Traeger, J. C. *Inorg. Chem.* **1993**, *32*, 2626–2629. (c) Bitsch, F.; Dietrich-Bucherker, C. O.; Khémis, A. K.; Sauvage, J. P.; Van Dorsselaer, A. *J. Am. Chem. Soc.* **1991**, *113*, 4023–4025. (d) Marquis-Rigault, A.; Dupont-Gervais, A.; Baxter, P. N. W.; Van Dorsselaer, A. *Inorg. Chem.* **1996**, *35*, 2307–2310.

(10) (a) Arakawa, R.; Matsuo, T.; Nozaki, K.; Ohno, T.; Haga, M. *Inorg. Chem.* **1995**, *34*, 2464–2467.

(11) (a) Jacquet, L.; Kirsch-De Mesmaeker, A. *J. Chem. Soc., Faraday Trans.* **1992**, *88* (17), 2471–2480. (b) Ortman, I.; Didier, P.; Kirsch-De Mesmaeker, A. *Inorg. Chem.* **1995**, *34*, 3695–3704. (c) Kirsch-De Mesmaeker, A.; Lecomte, J. P.; Kelly, J. M. *Topics in Current Chemistry-Electron Transfer II*, Vol. 177; J. Mattay, Springer Verlag: Berlin, 1996; pp 25–76.



**Figure 1.** Electrospray mass spectrum of compound A in  $\text{CH}_2\text{Cl}_2$  at  $V_c = 10$  V. The inset shows the resolution of the peak at  $m/z$  1593 (isotopic peaks separated by 0.3  $m/z$  units).

$\text{Ru}(\text{phen})_2\text{Cl}_2$  (phen = 1,10-phenanthroline) pretreated with  $\text{AgNO}_3$ , reacts with  $\text{Ru}(\text{HAT})_3^{2+}$  (6:1 ratio) during 48 h, to give rise to  $[\text{Ru}(\text{HAT})_3[\text{Ru}(\text{phen})_2]_6]^{14+}$ , isolated by precipitation with ammonium hexafluorophosphate.<sup>12</sup>

The heptametallic complex  $\text{Ru}(\text{HAT})_3[\text{Ru}(\text{phen})_2]_6(\text{PF}_6)_4$  ( $[\text{M}]$  in ESMS, 5602.2 Da) in dichloromethane or acetonitrile is directly analyzed by ESMS<sup>13</sup> (Figure 1).

For all the peaks, the width and the shape of the unresolved isotopic pattern are in good agreement with the simulated ones (24 Da at 10% from the base). The following widths ( $m/z$  units) are respectively measured for the ions with 3, 4, 5, and 6 charges: 8.3 (calcd 8.0), 6.5 (calcd 6.0), 5.2 (calcd 4.8), and 4.1 (calcd 4.0). The peak at 1593 has been resolved (inset of Figure 1), confirming that the ion is triply charged (isotopic peaks separated by 0.3  $m/z$  units).

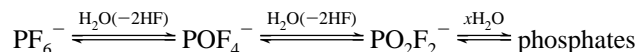
The spectrum is dominated by four sets of peaks with four different states of charge ( $z$ ). Peaks at  $m/z = 1635$ , 1593, and 1548 can be assigned to triply charged species ( $[\text{M} - 7\text{PF}_6^- +$

(12) To a solution of  $\text{Ru}(\text{phen})_2\text{Cl}_2$  (0.039 g, 0.074 mmol) in absolute ethanol (11 mL) is added solid  $\text{AgNO}_3$  (0.032 g, 0.019 mmol). After 2.5 h of stirring at room temperature,  $\text{Ru}(\text{HAT})_3\text{Cl}_2$  in ethylene glycol (5 mL) is added, and the mixture is refluxed for 48 h. After removal of  $\text{AgCl}$  by repeated centrifugation, an excess of solid  $\text{NH}_4\text{PF}_6$  is added to the mother liquor and the aubergine-purple precipitate is filtered out and dried over  $\text{P}_2\text{O}_5$ . The crude product is dissolved in acetonitrile, and ethanol is added in order to induce the precipitation of the complex: 0.044 g (64% yield). Elemental analysis: Calcd including  $20\text{H}_2\text{O}$ : C, 36.3; H, 2.6; N, 10.0. Found: C, 36.6; H, 2.6; N, 10.7. UV/vis spectrum (in acetonitrile):  $\lambda_{\text{max}}$  (nm) ( $\epsilon/\text{M}^{-1}\text{cm}^{-1}$ ): 398 ( $7.4 \times 10^4$ ), 576 ( $7.7 \times 10^4$ ). Luminescence (in acetonitrile):  $\lambda_{\text{max}} > 800$  nm.

(13) Positive ES mass spectra were obtained on a VG BIO-Q triple-quadrupole mass spectrometer with a mass to charge ( $m/z$ ) range of 4000 (Micromass, Altrincham, U.K.). The ES interface was heated to 50 °C. The sampling cone voltage ( $V_c$ ) varied from 10 to 70 V. The sample was dissolved in dichloromethane or acetonitrile ( $10^{-5}$  M). Sample solutions were introduced into the mass spectrometer source with a Harvard type 55 1111 syringe pump (Harvard Apparatus, South Natick, MA) with a flow rate of 4  $\mu\text{L}/\text{min}$ . The resolution was usually about 700 at  $m/z$  700, except for the determination of the state of charge for the peak at  $m/z = 1593$ . In this latter case, a MaxEnt Reconstruction (Micromass, Altrincham, U.K.) was used. A PEEK capillary tube (Upchurch Scientific, Oak Harbor, MA) was used rather than a fused silica capillary to avoid any interactions with the samples.

$\text{HPO}_4^{2-} + \text{POF}_4^- + \text{PO}_2\text{F}_2^-]^{3+}$ ,  $[\text{M} - 10\text{PF}_6^- + \text{HPO}_4^{2-} + \text{POF}_4^- + 4\text{PO}_2\text{F}_2^-]^{3+}$ , and  $[\text{M} - 10\text{PF}_6^- + 2\text{HPO}_4^{2-} + 3\text{PO}_2\text{F}_2^-]^{3+}$ ). Similarly, peaks at  $m/z = 1190$ , 1158, and 1126 correspond to  $[\text{M} - 8\text{PF}_6^- + \text{HPO}_4^{2-} + \text{POF}_4^- + \text{PO}_2\text{F}_2^-]^{4+}$ ,  $[\text{M} - 11\text{PF}_6^- + \text{HPO}_4^{2-} + \text{POF}_4^- + 4\text{PO}_2\text{F}_2^-]^{4+}$ , and  $[\text{M} - 11\text{PF}_6^- + 2\text{HPO}_4^{2-} + 3\text{PO}_2\text{F}_2^-]^{4+}$ , respectively. The 5+ ion at  $m/z = 897$  ( $[\text{M} - 12\text{PF}_6^- + \text{HPO}_4^{2-} + \text{POF}_4^- + 4\text{PO}_2\text{F}_2^-]^{5+}$ ) is also accompanied by two peaks at  $m/z = 923$  ( $[\text{M} - 9\text{PF}_6^- + \text{HPO}_4^{2-} + \text{POF}_4^- + \text{PO}_2\text{F}_2^-]^{5+}$ ) and  $m/z = 871$  ( $[\text{M} - 12\text{PF}_6^- + 2\text{HPO}_4^{2-} + 3\text{PO}_2\text{F}_2^-]^{5+}$ ). Finally, the spectrum exhibits three peaks corresponding to 6+ charged moieties at  $m/z = 745$ , 723, and 702 ( $[\text{M} - 10\text{PF}_6^- + \text{HPO}_4^{2-} + \text{POF}_4^- + \text{PO}_2\text{F}_2^-]^{6+}$ ,  $[\text{M} - 13\text{PF}_6^- + \text{HPO}_4^{2-} + \text{POF}_4^- + 4\text{PO}_2\text{F}_2^-]^{6+}$ , and  $[\text{M} - 13\text{PF}_6^- + 2\text{HPO}_4^{2-} + 3\text{PO}_2\text{F}_2^-]^{6+}$ , respectively).<sup>14</sup>

Formation of  $\text{POF}_4^-$ ,  $\text{PO}_2\text{F}_2^-$ , and phosphates, resulting from the hydrolysis of  $\text{PF}_6^-$ , has already been described in the literature with other transition metals.<sup>15,16</sup>



ESMS seems to lead to a selective counterion loss. Indeed, the loss of a dianion ( $\text{HPO}_4^{2-}$ ) is less favorable than the loss of a monoanion ( $\text{PF}_6^-$ ). Moreover, the ions pairs formed with  $[\text{Ru}_7]^{14+}$  and  $x\text{PO}_2\text{F}_2^-$  or  $x\text{POF}_4^-$  appear also as more stable under the electrospray conditions than the pairs  $[\text{Ru}]^{14+} + x(\text{PF}_6^-)$ . It should be stressed that this ion pairing with hydrolyzed  $\text{PF}_6^-$  seems to be typical of complexes with a HAT as a central bridging ligand chelated to 2 or 3  $\text{Ru}(\text{L})_2^{2+}$  units.<sup>17</sup>

Consequently, all of the peaks observed in the ES spectrum correspond to a single heptametallic Ru(II) complex associated with different types of counteranions.

In conclusion, the ESMS brings clearcut evidences for the nuclearity of the heptametallic Ru(II) complex which is thus univocally characterized. This technique can be regarded as extremely valuable to prove the existence of very large polynuclear transition metal complexes. Moreover, the preparation of A offers the possibility to synthesize larger three-dimensional polymetallic dendrimers if the terminal phen's are replaced by trischelating HAT's.

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(14) Actually, as the mass of  $1\text{PF}_6^- + 1\text{PO}_2\text{F}_2^- = 2\text{POF}_4^-$ , other combinations of counterions can be given. The one containing the highest number of  $\text{PF}_6^-$  has been chosen.

(15) (a) Fernandez-Galan, R.; Manzano, B. R.; Otero, A.; Lanfranchi, M.; Pellinghelli, M. A. *Inorg. Chem.* **1994**, *33*, 2309–2312 and references therein.

(16) Hydrolysis could take place during the isolation procedure. <sup>19</sup>F and <sup>31</sup>P NMR measurements reveal the presence of  $\text{PF}_6^-$  only. However, in NMR, it is of course the total amount of  $\text{PF}_6^-$  which is measured, thus also some excess of  $\text{KPF}_6$ , so that the amount of hydrolyzed  $\text{PF}_6^-$  could be negligibly small versus the global  $\text{PF}_6^-$  content.

(17) Leize, E.; Van Dorsselaer, A.; Ortman, I.; Kirsch-De Mesmaeker, A. Manuscript in preparation.