Inorganica Chimica Acta
LETTER

A heptanuclear ruthenium(II) polypyridine complex: synthesis, absorption spectrum, luminescence, electrochemical behavior

Gianfranco Denti*
Istituto di Chimica Agraria, Universita' di Pisa, I-56124 Pisa (Italy)

Sebastiano Campagna*
Dipartimento di Chimica Inorganica e Struttura Molecolare dell'Universita', I-98166 Messina (Italy)

Luigina Sabatino, Scolastica Serroni
Dipartimento di Chimica, Universita' della Calabria, I-87030 Rende (Italy)

Mauro Ciano and **Vincenzo Balzani***
Istituto FRAE-CNR and Dipartimento di Chimica 'G. Ciamician' dell'Universita', I-40126 Bologna (Italy)

(Received June 25, 1990)

Assembly of molecular components that exhibit specific properties and contain appropriate 'pieces of information' can be used to build up supramolecular species capable of performing useful functions [1, 2]. In particular, assembly of luminescent and redox-reactive components may lead to photochemical molecular devices [3] capable of performing light induced energy migration or charge separation processes which are at the basis of important applications, including natural [4] and artificial [5] solar energy conversion. Mononuclear Ru(II) polypyridine complexes are well known luminescent and redox-reactive molecules [6] that can be assembled in supramolecular structures [7, 8]. Bridging ligands like 2,3-bis(2-pyridyl)pyrazine (dpp) are quite suitable in this regard [9–14] since they allow us to use a 'complexes as ligands' strategy to obtain compounds of high nuclearity. In previous papers we reported the synthesis and properties of trinuclear [12, 14] and tetranuclear [13, 14] luminescent and redox-reactive complexes. We have now synthesized the luminescent and redox-reactive heptanuclear complex $Ru[(\mu\text{-dpp})Ru(bpy)(\mu\text{-dpp})Ru(bpy)_2]_3{}^{14+}$ (**5**). To our knowledge, no luminescent and redox-reactive coordination compound with nuclearity higher than four has previously been reported.

Experimental

$RuCl_3$ (**1**) and the 'complex ligand' $Ru(bpy)(dpp)_2{}^{2+}$ (**2**) [14] were refluxed in ethanol for 24 h in the presence of trifluoroacetic acid (1 equiv.) to obtain the new tetranuclear complex $Ru[(\mu\text{-dpp})Ru(bpy)(dpp)]_3{}^{8+}$ (**3**). The subsequent step for the synthesis of **5**, illustrated in Fig. 1, was carried out refluxing **3** with $Ru(bpy)_2Cl_2$ (**4**) in ethanol for 72 h. Each complex was purified and reacted in the chloride form, but characterized as the hexafluorophosphate salt. The purification of the mono- and tetranuclear complexes was carried out by ion-exchange chromatography on Sephadex-CM C-25 resin, using as eluant a solution of NaCl in 5:3 (vol./vol.) water/acetone; the orange–brown monometallic complex passed with salt concentration 0.1 M, the violet tetrametallic compound with 0.3 M. Sodium chloride was then separated by several successive extractions with ethanol/acetone. The highly charged dark-violet heptametallic species was purified by several recrystallizations from acetonitrile/ethanol; analytical scale ion-exchange chromatography was used in order to confirm the absence of the tetrametallic precursor in the final sample. All products gave consistent elemental analyses, IR and conductivity data. In particular, the IR spectrum of the tetranuclear complex showed the features typical [14] of the presence of dpp both as terminal and bridging group. It should be considered that compounds **2**, **3** and **5** may be mixtures of optical and geometrical isomers. For compounds **2**, NMR measurements suggest that only one of the three possible geometrical isomers is present in our sample. For compounds **3** and **5** ^1H NMR spectra are very complicated. Crystals suitable for diffractometric analysis will only be obtained starting from an enantiomerically resolved precursor and by separating the diastereoisomeric products. Efforts in this direction are in course.

Results and discussion

Figure 2 shows the absorption spectrum and (in the inset) the luminescent spectrum of the heptanuclear complex **5**. Some spectroscopic, photophysical and electrochemical data are given in Table 1, where the analogous data previously reported for $Ru(bpy)_3{}^{2+}$ (**6**) [6], $(bpy)Ru[(\mu\text{-dpp})Ru(bpy)_2]_2{}^{6+}$ (**7**)

---

*Authors to whom correspondence should be addressed.

0020-1693/90/$3.50

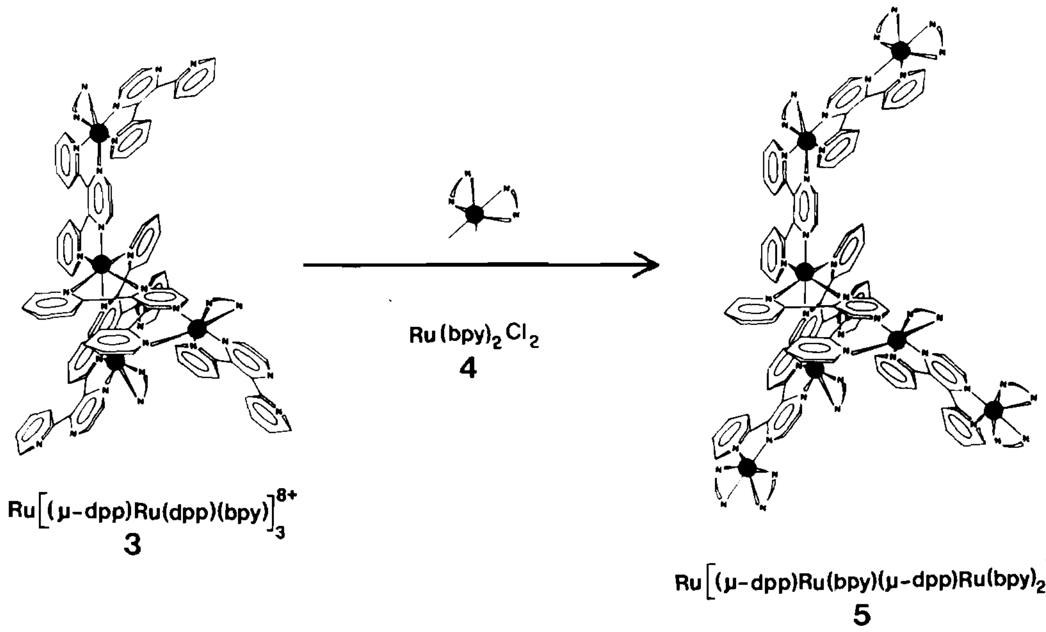

Fig. 1. Schematic representation of the last step of the synthesis of the heptanuclear complex 5.

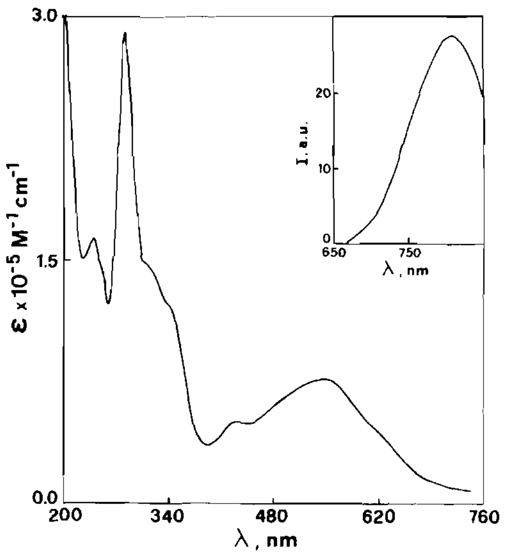

Fig. 2. Electronic absorption and (inset) luminescence spectra of 5 in acetonitrile solution at room temperature.

[12], and Ru[(μ-dpp)ru(bpy)$_2$]$_3^{8+}$ (8) [13] are also shown for comparison purposes. As one can see, 5 exhibits ligand-centered bands in the UV region and broad metal-to-ligand charge transfer bands in the visible region, much more intense than those of the previously reported [9b, 13] tetranuclear complex 8. The maximum of the luminescent band is at slightly higher energy than that of 8, and the luminescence lifetime is slightly longer. The corrected excitation spectrum in the visible shows that the luminescent level of 5 is populated with the same efficiency regardless of the excitation wavelength.

The 'complexes as ligands' approach used for the synthesis is also useful to identify the lowest MLCT excited state and the sites which are easier to oxidize and to reduce. Since bpy is a stronger σ-donor and a weaker π-acceptor than μ-dpp [9–14], the Ru ions easier to oxidize are those of the three peripheral (μ-dpp)Ru(bpy)$_2^{2+}$ units of 5. On electrochemical oxidation, the cyclic voltammogram of 5 shows a reversible tri-electronic wave, which indicates that the three peripheral Ru ions, as expected, are equivalent and do not appreciably communicate with each other. Oxidation of the other Ru^{2+} ions cannot be achieved in the potential window explored ($< +1.8$ V versus SCE). The pattern of the voltammograms on reduction is very complicated: a reversible tri-electronic wave is followed by an almost continuous succession of waves. A complicated reduction pattern was indeed expected since 5 contains as many as 21 dipyridine-type coordinating sites and it is known [6, 9–14] that each of them can undergo one electron reduction in the potential window $-0.5/-2.0$ V. It is also known that μ-dpp is much easier to reduce than bpy, and that, for the electronic reasons mentioned above, the four dpp-type coordinating sites which are present in each (μ-dpp)Ru(bpy)(μ-dpp)Ru(bpy)$_2^{4+}$ 'superligand' of the central Ru^{2+} core are not equivalent and become more and more difficult to reduce on moving from the center to the periphery. In their turn, the two bpy-type reduction

TABLE 1. Spectroscopic, photophysical and electrochemical data[a]

	Absorption λ_{max} (ϵ)[d] (nm)	Luminescence					Electrochemical[b]	
		298 K			77 K[c]		$E_{1/2}$ox	$E_{1/2}$red
		λ_{max} (nm)	τ (ns)	$\Phi \times 10^{-3}$	λ_{max} (nm)	τ (μs)		
5	547 (76.2)	808	80	0.9	725	2.0	+1.38[e]	−0.58[e]
6[f]	450 (13.0)	615	1100	59	582	4.8	+1.24	−1.26
7[g]	545 (23.5)	804	80	1.1	721	1.8	+1.48[g]	−0.55[h]
8[i]	545 (46.0)	811	60	1.0	727	1.4	+1.50[e]	−0.56[e]

[a] Deoxygenated acetonitrile solution at room temperature, unless otherwise noted. [b] Solutions containing 0.1 M tetraethylammonium perchlorate: only the potentials (V vs. SCE) of the first oxidation and reduction waves are reported. [c] MeOH/EtOH 4:1 (vol./vol.) rigid matrix. [d] 10^{-3} M^{-1} cm^{-1}. [e] Trielectronic wave. [f] Ref. 6. [g] Ref. 12. [h] Dielectronic wave. [i] Refs. 13 and 14.

sites present at the periphery of each 'superligand' are equivalent to each other but they are not equivalent to the internal bpy sites. Preliminary spectroelectrochemical experiments carried out at −0.80 V indicate that, as expected, the first reduction wave involves the dpp ligands (presumably, of the central metal core, see above). Luminescence likely originates from the lowest (proximate) metal-to-ligand CT levels which involve the peripheral Ru ions and their bridging dpp ligands.

Oligonuclear complexes like 5 are interesting because they accumulate many chromophoric and redox centers in the same supramolecular entity and exhibit luminescence from a relatively long-lived excited state. They are promising as (i) antenna components in photochemical molecular devices [3], e.g. for spectral sensitization of semiconductor electrodes [15]; (ii) multi-electron transfer photosensitizers [10, 11]; and, perhaps, (iii) luminescent probes and photochemical cleavers for biological applications [16]. Finally, the synthesis of 5 highlights the outstanding possibilities offered by the 'complexes as ligands' synthetic strategy which can be considered a particularly interesting case of the structure-directed synthetic methods currently used to obtain large artificial molecules [17, 18].

Acknowledgements

We thank Dr F. Stillitani, Mr L. Minghetti and Mr G. Gubellini for technical assistance and the Consiglio Nazionale delle Ricerche (Progetto Finalizzato Chimica Fine II), Ministero della Pubblica Istruzione, and NATO (Grant No. 937/86) for financial support.

References

1 J. M. Lehn, *Angew. Chem., Int. Ed. Engl., 27* (1988) 89.

2 F. L. Carter, R. E. Siatkowski and H. Wohltjen (eds.), *Molecular Electronic Devices*, North Holland, Amsterdam, 1988.

3 V. Balzani (ed.), *Supramolecular Photochemistry*, Reidel, Dordrecht, 1987.

4 J. Deisenhofer and H. Michel, *Angew. Chem., Int. Ed. Engl., 28* (1989) 829.

5 J. S. Connolly and J. R. Bolton, in M. A. Fox and M. Chanon (eds.), *Photoinduced Electron Transfer*, Part D, Elsevier, Amsterdam, 1988, p. 303.

6 A. Juris, V. Balzani, F. Barigelletti, S. Campagna, P. Belser and A. von Zelewsky, *Coord. Chem. Rev., 84* (1988) 85.

7 T. J. Meyer, *Acc. Chem. Res., 22* (1989) 163.

8 F. Scandola, M. T. Indelli, C. Chiorboli and C. A. Bignozzi, *Topics Curr. Chem., 158* (1990) in press.

9 (a) K. J. Brewer, W. R. Jr. Murphy, S. R. Spurlin and J. D. Petersen, *Inorg. Chem., 25* (1986) 882; (b) W. R. Jr. Murphy, K. J. Brewer, G. Gettliffe and J. D. Petersen, *Inorg. Chem., 28* (1989) 81.

10 C. H. Braustein, A. D. Baker, T. C. Strekas and H. D. Gafney, *Inorg. Chem., 23* (1984) 857; Y. Fuchs, S. Lofters, T. Dieter, W. Shi, R. Morgan, T. C. Strekas, H. D. Gafney and A. D. Baker, *J. Am. Chem. Soc., 109* (1987) 2691.

11 K. Kalyanasundaram and Md. K. Nezeeruddin, *Chem. Phys. Lett., 158* (1989) 45.

12 S. Campagna, G. Denti, L. Sabatino, S. Serroni, M. Ciano and V. Balzani, *Gazz. Chim. Ital., 119* (1989) 415.

13 S. Campagna, G. Denti, L. Sabatino, S. Serroni, M. Ciano and V. Balzani, *J. Chem. Soc., Chem. Commun.*, (1989) 1500.

14 G. Denti, S. Campagna, L. Sabatino, S. Serroni, M. Ciano and V. Balzani, *Inorg. Chem.*, in press.

15 N.Vlachopulos, P. Liska, J. Augustynski and M. Graetzel, *J. Am. Chem. Soc., 110* (1988) 1216; R. Dabestani, A. J. Bard, A. Campion, M. A. Fox, T. E. Mallouk, S. E. Webber and J. M. White, *J. Phys. Chem., 92* (1988) 1872; R. Amadelli, R. Argazzi, C. A. Bignozzi and F. Scandola, *J. Am. Chem. Soc.*, in press.

16 A. B. Tossi and J. M. Kelly, *Photochem. Photobiol., 49* (1989) 545; A. M. Pyle, J. P. Rehmann, R. Mesheyer, C. V. Kumar, N. J. Turro and J. K. Barton, *J. Am. Chem. Soc., 111* (1989) 3051.

17 F. H. Konkhe, J. P. Mathias and J. F. Stoddart, *Angew. Chem., Int. Ed. Engl., 28* (1989) 1103.

18 D. A. Tomalia, A. M. Naylor and W. A. Goddard III, *Angew. Chem., Int. Ed. Engl., 29* (1990) 138.