

## ELECTRONIC ABSORPTION SPECTRUM AND REDUCTION BEHAVIOR OF A MULTICOMPONENT, TRINUCLEAR Ru(II) SPECIES CONTAINING 2,3-BIS(2'-PYRIDYL)PYRAZINE BRIDGING LIGANDS AND 2,2'-BIQUINOLINE PERIPHERAL LIGANDS

Frédérique LOISEAU<sup>1,\*</sup>, Scolastica SERRONI<sup>2,\*</sup> and Sebastiano CAMPAGNA<sup>3,\*</sup>

*Dipartimento di Chimica Inorganica, Chimica Analitica e Chimica Fisica,*

*Università di Messina, Via Sperone 31, 98166 Messina, Italy;*

*e-mail: <sup>1</sup> f.loiseau@chem.unime.it, <sup>2</sup> serroni@chem.unime.it, <sup>3</sup> photochem@chem.unime.it*

Received May 23, 2003

Accepted July 31, 2003

*Dedicated to Professor Sergio Roffia, with gratitude.*

Electronic absorption spectrum and reduction pattern of a trinuclear Ru(II) species containing 2,3-bis(2'-pyridyl)pyrazine bridging ligands and 2,2'-biquinoline peripheral ligands have been studied and compared with other multinuclear metal complexes of the same family of systems. The structural formula of the compound investigated is  $[\text{RuCl}_2\{\text{Ru}(\text{biq})_2(\mu\text{-}2,3\text{-dpp})_2\}]^{4+}$  (**1**; biq = 2,2'-biquinoline, 2,3-dpp = 2,3-bis(2'-pyridyl)pyrazine). The electronic absorption spectrum of **1** (in acetonitrile) is dominated by intense spin-allowed ligand-centred bands in the UV region and by moderately intense spin-allowed metal-to-ligand charge-transfer bands in the visible. The studied compound undergoes several quasireversible reduction processes in the potential window investigated (up to  $-1.20$  V vs SCE in DMF): two successive one-electron reductions at  $-0.52$  and  $-0.61$  V, followed by two processes involving two closely-spaced one-electron reductions each. Extensive comparison with reduction patterns of closely related species allows to assign each process to specific subunits of the multicomponent array. The effect of the peripheral biq ligands on the electronic interaction between inner subunits is evidenced.

**Keywords:** Ruthenium complexes; Redox behavior; Reductions; Multinuclear complexes; Polypyridine ligands; Bipyridines; UV spectroscopy; Voltammetry; Electrochemistry.

Multinuclear Ru(II) polypyridine complexes based on the 2,3-bis(2'-pyridyl)pyrazine (2,3-dpp) bridging ligand received much interest in the last decade from several viewpoints. For example, dendritic species made of this type of building blocks have been designed to play the role of artificial light-harvesting antenna species for solar energy conversion and as multielectron storage systems, because of (i) their ability to absorb a significant fraction of solar light and the occurrence of fast and efficient intercomponent energy

transfer processes within the multinuclear arrays<sup>1</sup>, and (ii) the possibility of exchanging a predetermined number of electrons in a reversible manner at accessible potentials<sup>2</sup>. The potential of this class of compounds is also due to the synthetic procedure employed, named “complexes as ligands/complexes as metals” (clcm), which is based on a modular approach<sup>3,4</sup>, allowing preparation of high nuclearity species (compounds containing as many as 22 metal centres have been obtained<sup>3b,3c</sup>) of controlled topology. For this synthetic approach to be effective, relatively large multinuclear synthons, both of “complex-ligand” and “complex-metal” nature, must be synthesized and their properties clarified. Among the various complexes-as-metal synthons used, trinuclear species of general formulas  $\{[M(\text{bpy})_2(\mu\text{-}2,3\text{-dpp})]_2M'\text{Cl}_2\}^{4+}$  (bpy = 2,2'-bipyridine; M = Ru(II) or Os(II); M' = Ru(II) or Os(II)) have been employed extensively and their redox properties have been investigated<sup>3a,5</sup>.

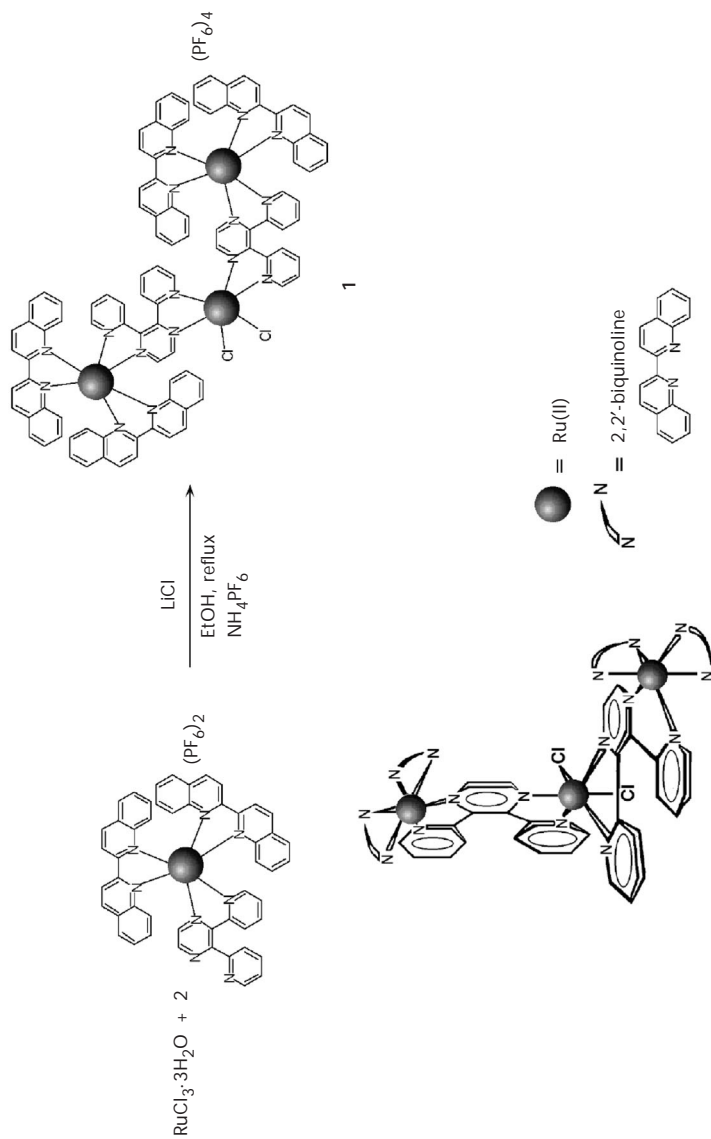
Some time ago we prepared the trinuclear species  $[\text{RuCl}_2\{\text{Ru}(\text{biq})_2(\mu\text{-}2,3\text{-dpp})\}_2]^{4+}$  (**1**, biq = 2,2'-biquinoline; for the synthesis and structural formula, see Scheme 1), belonging to the same series of trinuclear complexes mentioned above, with the notable difference that biq ligands replaced bpy as peripheral ligands. We used **1** for syntheses of two decanuclear compounds<sup>3a</sup>. However, electrochemistry of this species has never been investigated in detail, although it could be foreseen that the reduction properties of **1** are extremely rich and interesting since the biq ligands are known to reduce at less negative potentials than bpy ligands in Ru(II) complexes. Here we report a detailed investigation of the reduction properties of **1**, together with the new synthetic procedure used for its preparation, and the study of its electronic absorption spectrum.

## EXPERIMENTAL

### Materials and Methods

$[\text{RuCl}_2(\text{biq})_2]$  (ref.<sup>6</sup>) and  $[\text{Ru}(\text{biq})_2(2,3\text{-dpp})](\text{PF}_6)_2$  (ref.<sup>7</sup>) were prepared according to literature. All reactions, manipulations and measurements were performed in light-protected vessels.

TOF-SIMS measurements were performed in “static mode” (less than  $5 \times 10^{11}$  primary ions/cm<sup>2</sup>) in a TOF-SIMS IV (ION-TOF) instrument using a pulsed gallium beam (25 keV, 1 pA, 0.8 ns pulse width). Samples were prepared as very thin layers by microsyringe deposition of an acetonitrile solution of etched silver. Electronic absorption spectra were recorded on a Jasco V-560 spectrophotometer. Electrochemical measurements were carried out in argon-purged DMF at room temperature with a PAR 273 multipurpose equipment interfaced to a PC. The working electrode was a glassy carbon disk (8 mm<sup>2</sup>, Amel). The counter electrode was a Pt wire, and the reference electrode was an SCE separated with a fine glass frit.



The concentration of the complexes was about  $5 \times 10^{-4}$  mol dm<sup>-3</sup>. Tetrabutylammonium hexafluorophosphate was used as supporting electrolyte; its concentration was  $5 \times 10^{-2}$  mol dm<sup>-3</sup>. Cyclic voltammograms were obtained at scan rates of 20, 50, 200 and 500 mV s<sup>-1</sup>. For reversible processes, half-wave potentials (*vs* SCE) were calculated as the average of the cathodic and anodic peak potentials. The criteria for reversibility were the separation of 60 mV between cathodic and anodic peaks, the close to unity ratio of the cathodic and anodic peak currents, and the constancy of the peak potential on changing scan rate. The number of exchanged electrons was measured with differential pulse voltammetry (DPV) performed with scan rate of 20 mV s<sup>-1</sup>, pulse height of 75 mV, and duration of 40 ms, and by taking advantage of the presence of ferrocene used as the internal reference.

Experimental uncertainties are as follows: absorption maxima,  $\pm 2$  nm; molar absorption coefficients, 10%; redox potentials,  $\pm 10$  mV.

#### Synthesis of [RuCl<sub>2</sub>{(μ-2,3-dpp)Ru(biq)<sub>2</sub>}<sub>2</sub>](PF<sub>6</sub>)<sub>4</sub> (1)

A stirred solution of RuCl<sub>3</sub>·3H<sub>2</sub>O (12 mg, 0.046 mmol), [Ru(biq)<sub>2</sub>(2,3-dpp)](PF<sub>6</sub>)<sub>2</sub> (104 mg, 0.091 mmol) and excess LiCl in ethanol (20 ml) was refluxed for 4 days. The mixture was then cooled to room temperature, and an excess of solid NH<sub>4</sub>PF<sub>6</sub> was added. The obtained precipitate was filtered off and dissolved in the smallest amount of acetonitrile. The solution was chromatographed on Sephadex CM-15 for gel-filtration and, successively, on neutral alumina (column 20 × 2 cm). Using a mixture CH<sub>3</sub>CN/toluene 1:1 as eluent, the unreacted mononuclear precursor was removed, and the trinuclear product was obtained using a mixture MeOH/toluene 1:1 as eluent. This last fraction was evaporated to dryness and redissolved in acetonitrile. The product was recovered by precipitation in diethyl ether as a blue-violet powder that was washed several times with diethyl ether and dried *in vacuo*. Yield 67%. TOF-SIMS, *m/z*: 2303 [M - PF<sub>6</sub>]<sup>+</sup>, 1079 [M - 2 PF<sub>6</sub>]<sup>2+</sup>, 671 [M - 3 PF<sub>6</sub>]<sup>3+</sup>. For C<sub>100</sub>H<sub>68</sub>Cl<sub>2</sub>F<sub>24</sub>N<sub>16</sub>P<sub>4</sub>Ru<sub>3</sub> (2448.1) calculated: 49.07% C, 2.80% H, 9.16% N; found: 48.84% C, 2.63% H, 9.01% N.

## RESULTS AND DISCUSSION

The synthetic procedure for complex **1** is based on the “clcm” approach<sup>4</sup>. The species [Ru(biq)<sub>2</sub>(2,3-dpp)]<sup>2+</sup> is used as a complex-ligand, by taking advantage of the free chelating site present on the 2,3-dpp ligand, to connect another metal centre (Scheme 1). In the synthesis, an excess of LiCl is necessary to avoid formation of the undesired tetranuclear species [(μ-2,3-dpp)<sub>3</sub>Ru]<sup>8+</sup>.

The electronic absorption spectrum of complex **1** (Table I, Fig. 1) is dominated by strong absorption bands in the UV region and by moderately intense bands in the visible. The UV bands are attributed to spin-allowed ligand-centred transitions: in particular, the peak at 266 nm and the broad absorption around 320 nm belong to biq-centred transitions (together with the narrow band at 380 nm), by comparison with absorption bands of other biq-containing Ru(II) complexes<sup>8</sup>. Dpp-centred transitions are usually less intense than biq-centred ones and are known to lie around 360 nm;

TABLE I  
Electrochemical and UV-VIS spectroscopic data for complexes **1** to **5**

Complex	Formula	$E_{1/2}(\text{red}), \text{V vs SCE}^a$	$\lambda_{\text{max}}, \text{nm}$ ( $\epsilon \times 10^{-3}, \text{l mol}^{-1} \text{cm}^{-1}$ )
<b>1</b> <sup>b</sup>	$\{(\text{biq})_2\text{Ru}(\mu\text{-}2,3\text{-dpp})\}_2\text{RuCl}_2]^{4+}$	-0.52 [1]; -0.61 [1]; -0.82 [2] <sup>c</sup> ; -1.14 [2] <sup>d</sup>	266 (118.9); 324 (76.3); 380 (57.0); 545 (19.2); 625 (22.8); 751 (16.4)
<b>2</b> <sup>e,f</sup>	$[(\text{biq})_2\text{Ru}(\mu\text{-}2,3\text{-dpp})\text{Ru}(\text{biq})_2]^{4+}$	-0.45 [1]; -0.81 [2]; -0.95 [1]; -1.19 [2]	537 (15.6)
<b>3</b> <sup>e,g</sup>	$\{(\text{bpy})_2\text{Ru}(\mu\text{-}2,3\text{-dpp})\}_2\text{RuCl}_2]^{4+}$	-0.72 [1]; -0.88 [1]	283 (111.3); 434 (21.1); 494 (19.7); 625 (26.1)
<b>4</b> <sup>e,g</sup>	$\{(\text{bpy})_2\text{Ru}(\mu\text{-}2,3\text{-dpp})\}_2\text{Ru}(\text{bpy})]^{6+}$	-0.52 [1]; -0.66 [1]; -1.13 [1]; -1.23 [1]	282 (193.4); 425 (35.7); 545 (23.5)
<b>5</b> <sup>e,g</sup>	$\{(\text{bpy})_2\text{Ru}(\mu\text{-}2,3\text{-dpp})\}_2\text{OsCl}_2]^{4+}$	-0.71 [1]; -0.96 [1]	224 (113.5); 436 (22.3); 620 (24.9)

<sup>a</sup> The number of exchanged electrons is given in square brackets. <sup>b</sup> Electrochemical data in argon-purged DMF solution and spectroscopic data in acetonitrile solution. <sup>c</sup> This value refers to a single peak in DPV experiments, which is larger than expected for two one-electron processes involving non-interacting sites (a similar comment could be made on the separation between cathodic and anodic waves in cyclic voltammograms). Thus, the two redox sites are very weakly interacting with each other but in a non-sizeable manner. <sup>d</sup> Two closely-spaced one-electron processes. The average value is obtained from the cyclic voltammograms. However, in DPV experiments it appears that the separation between the two processes is here significantly larger than in the previous reduction process(es). <sup>e</sup> In argon-purged acetonitrile solution. <sup>f</sup> From ref.<sup>7</sup>. <sup>g</sup> From ref.<sup>5</sup>

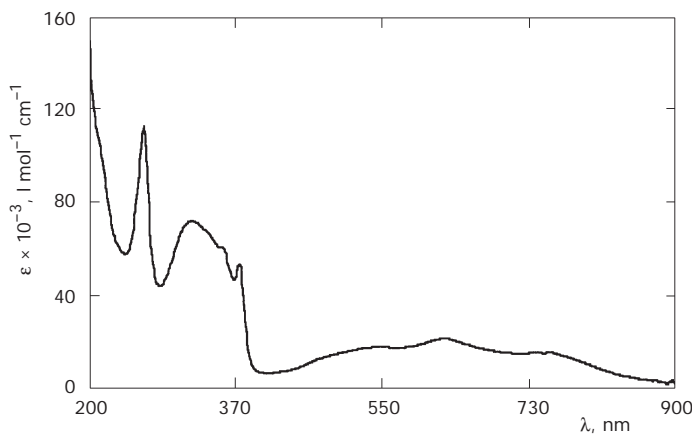


FIG. 1  
UV-VIS absorption spectrum of **1** in acetonitrile

hence, they are probably obscured by the more intense biq-based transitions. The bands that appear in the visible region, are attributed to spin-allowed metal-to-ligand charge-transfer (MLCT) transitions. In particular, the band with absorption maximum at about 750 nm is attributed to RuCl<sub>2</sub>-to-dpp CT transitions. Actually, it is known that in this series of complexes the central metal, carrying two chloride ligands, is easier to oxidize than the peripheral metal centres. Therefore, the lowest-lying MLCT state involves the central Ru(II) centre. Peripheral Ru-to-biq and Ru-to-dpp CT transitions give rise to the absorption features peaking at 625 and 545 nm, respectively.

Cyclic and differential pulse voltammetry (Table I, Fig. 2) of complex **1** both show several reduction processes. The first two steps involve one electron each, the third one being apparently bielectronic (although separation between cathodic and anodic waves is somewhat larger than expected for non-interacting sites). The fourth and fifth processes are again mono-electronic, although so closely-spaced that we have not been able to assign specific potential to each one of them. At potentials more negative than -1.20 V vs SCE, other processes occur, but they are "ill-behaved" under our experimental conditions and will not be discussed here.

For discussing the reduction processes of **1**, it is useful to recall the reduction processes for three related species, [Ru(biq)<sub>2</sub>(μ-2,3-dpp)Ru(biq)<sub>2</sub>]<sup>4+</sup> (**2**)<sup>7</sup>, [{Ru(bpy)<sub>2</sub>(μ-2,3-dpp)}<sub>2</sub>RuCl<sub>2</sub>]<sup>4+</sup> (**3**)<sup>5</sup> and [{Ru(bpy)<sub>2</sub>(μ-2,3-dpp)}<sub>2</sub>Ru(bpy)]<sup>6+</sup> (**4**)<sup>5</sup>. Literature data for these species are given for acetonitrile, while **1** herein is studied in DMF; however, we are more interested in the sequence of processes than in absolute potential values, so discrepancies due to different solvents can be disregarded, for acetonitrile and DMF are not expected to interact in particularly specific way with the compounds under consideration. Compound **2** undergoes first monoelectronic cathodic step at -0.45 V, which has been assigned to first reduction of the bridging ligand. Successively, it undergoes a bielectronic transfer ( $E_{1/2} = -0.81$  V), which has been attributed to simultaneous one-electron reductions of two biq ligands belonging to different metal centres. A third cathodic process takes place at -0.95 V, assigned to second one-electron reduction of the 2,3-dpp bridge. Finally, a fourth process, bielectronic, takes place at -1.19 V, which is attributed to simultaneous one-electron reductions of the remaining biq ligands. The relevant information we can infer from the reduction properties of **2** is that the 2,3-dpp bridging ligand is reduced (by one electron) at less negative potentials than the first biq ligand belonging to each metal centre, and that the second reduction of the bridge occurs before reduction of the second biq ligand belonging to each metal. Comparison

between the first cathodic processes of **3** and **4** ( $-0.72$  and  $-0.52$  V, respectively), both attributed to the one-electron reduction of the 2,3-dpp bridging ligand, highlights the effect of the presence of chlorides: as expected, the reduction potential of the bridge moves to more negative values on passing from **4** to **3**, *i.e.* in the presence of chlorides. This suggests that the 2,3-dpp bridging ligands in **1** would be reduced at more negative potentials than the analogous ligands in **2**.

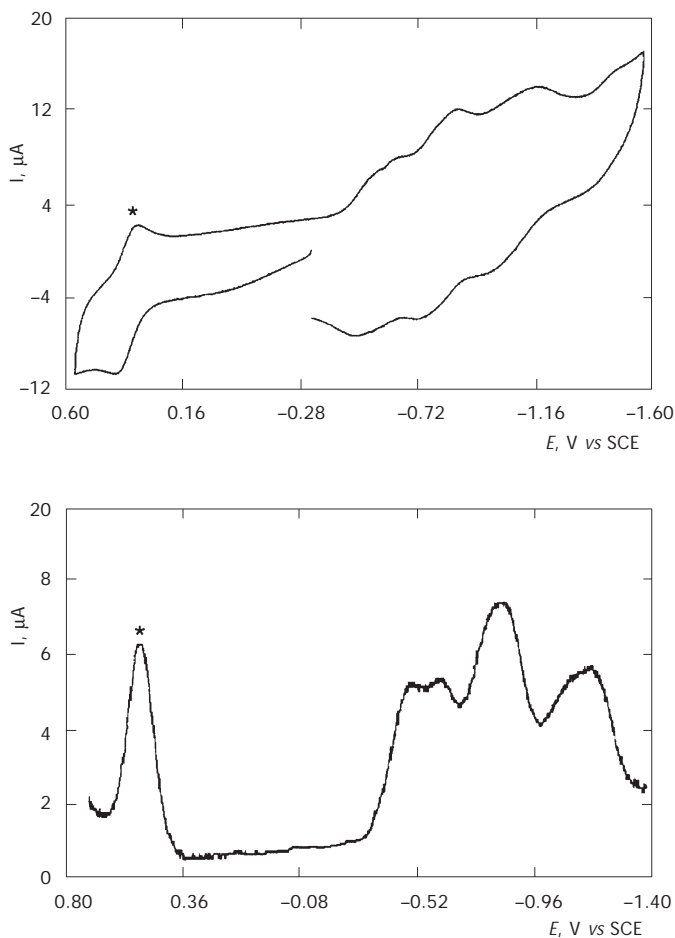


FIG. 2

Cyclic voltammogram (top) and differential pulse voltammogram (bottom) of **1** in argon-purged DMF solution. Scan rates are  $200 \text{ mV s}^{-1}$  for the CV and  $20 \text{ mV s}^{-1}$  for the DPV. Asterisk denotes the  $\text{Fc}/\text{Fc}^+$  redox couple

On the basis of the above discussion, the first two reduction processes (both monoelectronic) of **1** are attributed to successive one-electron reductions of the two 2,3-dpp bridging ligands. Their values (−0.52 and −0.61 V) are indeed slightly more negative than the reduction potential of the same ligand in **2**, as expected because of the effect of the chlorides. The successive reduction process, apparently involving two electrons, is attributed to the almost simultaneous one-electron reduction of two big ligands linked to different Ru(II) peripheral centres. The fourth and fifth processes are clearly closely-spaced one-electron reductions, as indicated by the differential pulse voltammogram (see Fig. 2), and are attributed to second reduction of each bridging ligand. The reduction potentials of the latter processes are closer to each other compared to the potentials corresponding to first reduction of the same subunits (see above). This result is in line with literature data on similar species, including **4** (ref.<sup>5</sup>). The reason is the decreased electronic interaction between the bridging ligands upon the first reduction, as a consequence of increased energy gap between (mono-reduced) bridging ligand-based orbitals,  $\pi_{BL}^*$ , and metal orbitals,  $\pi_M$ . The later parameter governs the superexchange interaction that promotes ligand–ligand interaction in Ru(II) polypyridine complexes<sup>9,10</sup>.

A result warranting a particular comment is the separation between the first two cathodic processes, identified as involving one-electron reduction of the two bridging ligands (see above), and therefore giving indirect information on the electronic interaction between these two subunits. This topic has already been discussed for another series of trinuclear representatives of this family. It has been stated that the potential separation is related to the energy difference between  $\pi^*$  ligand-based and  $\pi_M$  metal-based orbitals: at a larger energy difference, a smaller interaction (and therefore smaller separation between potentials) corresponds, in agreement with the superexchange theory. For example, for complex **4** the separation between the two ligand-based reduction is 0.16 V. Such separation increases, as expected, to 0.25 V in  $\{[\text{Ru}(\text{bpy})_2(\mu\text{-}2,3\text{-dpp})]_2\text{OsCl}_2\}^{4+}$  (**5**), since the Os-based  $\pi_M$  orbitals are higher-lying than the corresponding Ru-based orbitals, therefore promoting a stronger ligand–ligand interaction. Since (i) relevant orbitals on the central Ru metal of **1** are very close in energy to the corresponding orbitals of **3**, as indicated by oxidation potentials (for central Ru(II) of **1** and **3**, 0.86 and 0.82 V, respectively<sup>3a,5</sup>), and (ii) the bridging ligand orbitals in **1** are lower-lying than the same orbitals in **3** (reduction potentials are −0.52 and −0.72 V, respectively, Table I), one could expect a larger ligand–ligand interaction in **1** than in **3**, and, as a consequence, also a larger potential separation. On the contrary, the experimental potential



separation in **1** is 0.09 V (Table I), suggesting a reduced interaction. It should be considered, however, that to conform to the superexchange theory<sup>11-13</sup>, the energy separation between the potentials reflects the electronic interaction between identical, interacting sites in similar species only if the other parameters (Coulombic factors and distance between the redox sites, for example) are assumed to be constant within the series. While this assumption, in a first approximation, is probably valid for **3** and **5**, containing the same ligands, it is most likely not valid anymore comparing **1** and **3**. In fact, the biq peripheral ligands present in **1** have orbitals which are much closer in energy to the bridging ligand orbitals than the bpy peripheral ligands contained in **3**, and, therefore, can interact significantly with the bridging ligands. The doubly-degenerated LUMOs of **1**, although in a first approximation centred on the bridging ligands, can therefore receive non-negligible contributions also from the peripheral biq ligands. The consequence is that the effective distance between the redox-active sites responsible for the first two one-electron reduction processes in **1** is larger than that in **3**. Hence, electronic interaction becomes reduced, leading to a reduced splitting of the reduction potentials. This result is a clear example that peripheral subunits may perturb electronic interaction between inner subunits in this class of multinuclear metal complexes<sup>14</sup>. Theoretical calculations would be very useful to confirm our interpretation. Semiempirical calculations parametrized for transition metals (ZINDO-INDO/I) have indeed been employed to verify the electrochemical data of dinuclear metal complexes based on the dpp bridges<sup>2b</sup>. Extension of such studies to the present trinuclear compound has been planned.

## CONCLUSIONS

The reduction behavior of the multinuclear species  $[\{\text{Ru}(\text{biq})_2(\mu\text{-}2,3\text{-dpp})\}_2\text{-RuCl}_2]^{4+}$  (**1**) has been investigated in DMF, and the results have been compared to those for other multinuclear systems of the large family of 2,3-dpp-bridged multinuclear compounds. Compound **1** undergoes several reduction processes that have been assigned to specific sites of its structure. Moreover, the results have highlighted that peripheral subunits may perturb electronic interaction between inner subunits in this class of multinuclear metal complexes.

*This work has been supported by the MIUR (Ministero dell'Istruzione, dell'Università e della Ricerca) and by the University of Messina. F. Loiseau also wishes to thank the European Community for a Marie Curie fellowship grant.*

## REFERENCES AND NOTES

1. a) Balzani V., Campagna S., Denti G., Juris A., Serroni S., Venturi M.: *Acc. Chem. Res.* **1998**, *31*, 26, and references therein; b) Balzani V., Ceroni P., Juris A., Venturi M., Campagna S., Puntoriero F., Serroni S.: *Coord. Chem. Rev.* **2001**, *219–221*, 545; c) Campagna S., Di Pietro C., Loiseau F., Maubert B., McClenaghan N., Passalacqua R., Puntoriero F., Ricevuto V., Serroni S.: *Coord. Chem. Rev.* **2002**, *229*, 67.
2. a) Venturi M., Serroni S., Juris A., Campagna S., Balzani V.: *Top. Curr. Chem.* **1998**, *197*, 193; b) Marcaccio M., Paolucci F., Paradisi C., Roffia S., Fontanesi C., Yellowlees L. J., Serroni S., Campagna S., Denti G., Balzani V.: *J. Am. Chem. Soc.* **1999**, *121*, 10081; c) Juris A., Venturi M., Ceroni P., Balzani V., Campagna S., Serroni S.: *Collect. Czech. Chem. Commun.* **2001**, *66*, 1.
3. a) Denti G., Campagna S., Serroni S., Ciano M., Balzani V.: *J. Am. Chem. Soc.* **1992**, *114*, 2944; b) Campagna S., Denti G., Serroni S., Juris A., Venturi M., Ricevuto V., Balzani V.: *Chem. Eur. J.* **1995**, *1*, 211; c) Serroni S., Juris A., Venturi M., Campagna S., Resino Resino I., Denti G., Credi A., Balzani V.: *J. Mater. Chem.* **1997**, *7*, 1227.
4. Serroni S., Campagna S., Puntoriero F., Di Pietro C., Loiseau F., McClenaghan N. D.: *Chem. Soc. Rev.* **2001**, *30*, 367.
5. Puntoriero F., Serroni S., Licciardello A., Venturi M., Juris A., Ricevuto V., Campagna S.: *J. Chem. Soc., Dalton Trans.* **2001**, 1035.
6. Belser P., von Zelewsky A.: *Helv. Chim. Acta* **1980**, *63*, 1675.
7. Denti G., Campagna S., Sabatino L., Serroni S., Ciano M., Balzani V.: *Inorg. Chem.* **1990**, *29*, 4750.
8. Juris A., Balzani V., Barigelletti F., Campagna S., Belser P., von Zelewsky A.: *Coord. Chem. Rev.* **1988**, *84*, 85.
9. Giuffrida G., Campagna S.: *Coord. Chem. Rev.* **1994**, *135–136*, 517.
10. Ward M. D.: *Chem. Soc. Rev.* **1995**, *24*, 121.
11. a) Halpern J., Orgel L. E.: *Discuss. Faraday Soc.* **1960**, *29*, 32; b) McConnell H. M.: *J. Chem. Phys.* **1961**, *35*, 508.
12. a) Day P.: *Comments Inorg. Chem.* **1981**, *1*, 155; b) Miller J. R., Beitz J. V.: *J. Chem. Phys.* **1981**, *74*, 6746; c) Richardson D. E., Taube H.: *J. Am. Chem. Soc.* **1983**, *105*, 40; d) Creutz C.: *Prog. Inorg. Chem.* **1983**, *30*, 1; e) Bencini A., Ciofini I., Daul C. A., Ferretti A.: *J. Am. Chem. Soc.* **1999**, *121*, 11418.
13. a) Newton M. D.: *Chem. Rev. (Washington, D. C.)* **1991**, *91*, 767; b) Jordan K. D., Paddon-Row M. N.: *Chem. Rev. (Washington, D. C.)* **1992**, *92*, 395; c) Todd M. D., Nitzan A., Ratner M. A.: *J. Phys. Chem.* **1993**, *97*, 29.
14. An analogous example dealing with smaller systems, *i.e.* the effect of peripheral ligands on the extent of metal–metal interaction in polypyridine ligand-bridged dinuclear complexes, is discussed in ref.<sup>9</sup>.