A New Hetero-tetrametallic Complex of Ruthenium and Osmium: Absorption Spectrum, Luminescence Properties, and Electrochemical Behaviour

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A new hetero-tetrametallic complex, $Os[(\mu\text{-}2,3\text{-dpp})Ru(bpy)_2]_3{}^{8+}$ (**1**), where 2,3-dpp = bis(2-pyridyl)pyrazine and bpy = 2,2'-bipyridine, has been prepared from the reaction of $Os(2,3\text{-dpp})_3{}^{2+}$ with $Ru(bpy)_2Cl_2$: luminescence of (**1**) takes place from the central Os-containing core, which collects the energy absorbed by the peripheral Ru-containing chromophores (antenna effect).

Because of their outstanding photophysical and electrochemical properties, Ru^{II}- and Os^{II}-polypyridine complexes have been extensively used in the last ten years as luminescent species and as reactants or mediators in light-induced and light-generating electron transfer processes.[1] Most of the complexes studied so far are species containing only one metal centre. For a variety of applications, however, oligometallic luminescent and redox systems are expected to be more useful[2] and their design is currently an important research field.

The 2,3 and 2,5 isomers of bis(2-pyridyl)pyrazine (dpp) are suitable bridging ligands to built-up polymetallic complexes.[3—5] We have used these bridges and the well known 2,2'-bipyridine (bpy) and 2,2'-biquinoline (biq) ligands to synthesize a number of homo- and hetero-polymetallic complexes which exhibit quite interesting luminescent and redox properties. Here we wish to report on the hetero-tetrametallic complex $Os[(\mu\text{-}2,3\text{-dpp})Ru(bpy)_2]_3{}^{8+}$ (**1**) (Figure 1) and on its parent mononuclear complexes $Ru(2,3\text{-dpp})(bpy)_2{}^{2+}$ (**3**)[3,4] and $Os(2,3\text{-dpp})_3{}^{2+}$ (**2**). The homo-tetrametallic analogue of (**1**), $Ru[(\mu\text{-}2,3\text{-dpp})Ru(bpy)_2]_3{}^{8+}$ (**4**), recently studied by Petersen *et al.*,[5] has also been investigated.

The complex $[Ru(2,3\text{-dpp})(bpy)_2](PF_6)_2$ has been prepared following standard procedures. The complex $[Os(2,3\text{-dpp})_3](PF_6)_2$ has been prepared by refluxing $K_2OsCl_6\cdot 2H_2O$ and 2,3-dpp (molar ratio 1 : 4) in diethyleneglycol (yield 77%). The tetrametallic complexes $\{Ru[(\mu\text{-}2,3\text{-dpp})Ru(bpy)_2]_3\}(PF_6)_8$ and $\{Os[(\mu\text{-}2,3\text{-dpp})Ru(bpy)_2]_3\}(PF_6)_8$ have been obtained (yield: 67% and 74%, respectively) from the corresponding $M(2,3\text{-dpp})_3{}^{2+}$ core by refluxing with $Ru(bpy)_2Cl_2$ in absolute ethanol for 48 (**4**) or 24 h (**1**). The complexes were characterized by elemental analysis, i.r. spectra, and conductivity measurements. Structural characterization of the tetrametallic compounds by n.m.r. and *X*-ray single crystal diffractometry is presently prevented because the samples are mixtures of several diastereoisomeric species (each metal centre can have Λ or Δ configuration).

Figure 2 shows the absorption spectra in the visible region of the four complexes in acetonitrile solution at room temperature. The inset of the same figure shows the luminescence bands of the two Os-containing complexes under the same experimental conditions. Table 1 collects the electrochemical, absorption, and luminescence data. Some previously reported data for (**3**)[3,4] and (**4**)[5] are in reasonable agreement with our results if one considers that different solvents were used and some of the luminescence maxima were uncorrected for phototube response.

The most important results are those concerning the hetero-tetranuclear complex (**1**). Its electrochemical, spectroscopic, and photophysical behaviour can be interpreted on the basis of the behaviour of the parent complexes (**2**) and (**3**). On electrochemical oxidation, (**1**) shows a monoelectronic, reversible wave at +1.25 V, followed by a trielectronic, almost reversible wave at +1.55 V. On the basis of the oxidation potentials of (**2**) and (**3**) (Table 1), it is possible to assign the monoelectronic wave to oxidation of the central Os ion, and the trielectronic wave to oxidation of the three peripheral Ru ions. Spectroelectrochemical experiments confirmed that oxidation of (**1**) involves two successive steps, leading to the disappearance of the metal-to-ligand charge transfer (MLCT) bands involving Os and Ru, respectively. On electrochemical reduction, a series of three waves are present in the cyclovoltammogram of (**1**) (Table 1). The dpp ligand is easier to reduce than bpy [compare, *e.g.*, the reduction potentials of $Ru(2,3\text{-dpp})_3{}^{2+}$ [5] with those of $Ru(bpy)_3{}^{2+}$ [1]], and it is even more so when it plays the role of a bridging ligand. Therefore, the three reduction waves can be associated to the first one-electron reduction of the three dpp ligands. For potentials more negative than −1.35 V several overlapping waves are present, probably corresponding to the second one-electron reduction of the dpp ligands and to the first reduction of peripheral bpy.

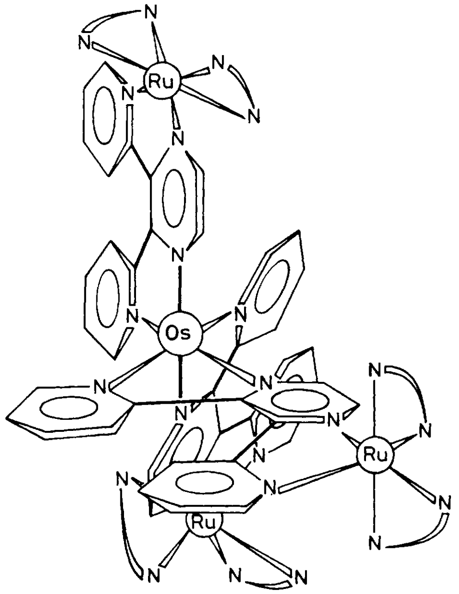

Figure 1. Schematic view of $Os[(\mu\text{-}2,3\text{-dpp})Ru(bpy)_2]_3{}^{8+}$ (**1**); N⌒N stands for bpy.

Table 1. Electrochemical, absorption, and emission data.

	Electrochemistry[a]		Absorption[b]	Luminescence[c]	
Complex	E_{ox}/V	E_{red}/V	λ_{max}/nm ($\varepsilon \times 10^{-3}$/mol^{-1} dm^3 cm^{-1})	298 K λ_{max}/nm (τ/ns)	77 K λ_{max}/nm (τ/μs)
(**1**)	+1.25; +1.55[d]	−0.55; −0.65; −0.77	428 (27.0); 549 (40.0)	875 (18)	802 (0.41)
(**2**)	+0.92	−0.84; −1.00; −1.36	475 (18.0)	768 (82)	729 (0.85)
(**3**)	+1.31[e]	−1.06; −1.50[e]	430 (12.0); 470 sh (11.5)	692 (276)	637 (4.1)
(**4**)	+1.50[d, f]	−0.56; −0.74; −0.89	422 (31.7); 545 (46.0)	819 (89)	728 (1.4)

[a] Acetonitrile solution containing 0.1 M tetraethylammonium perchlorate (TEAP), room temperature; potentials *vs.* standard calomel electrode. The waves are monoelectronic and reversible or almost reversible, unless otherwise noted. [b] Acetonitrile solution, room temperature. [c] Corrected emission maxima and luminescence lifetimes in deaerated acetonitrile solution (room temperature) or MeOH/EtOH 4:1 matrix (77 K). [d] Trielectronic wave. [e] Ref. 4. [f] Ref. 5.

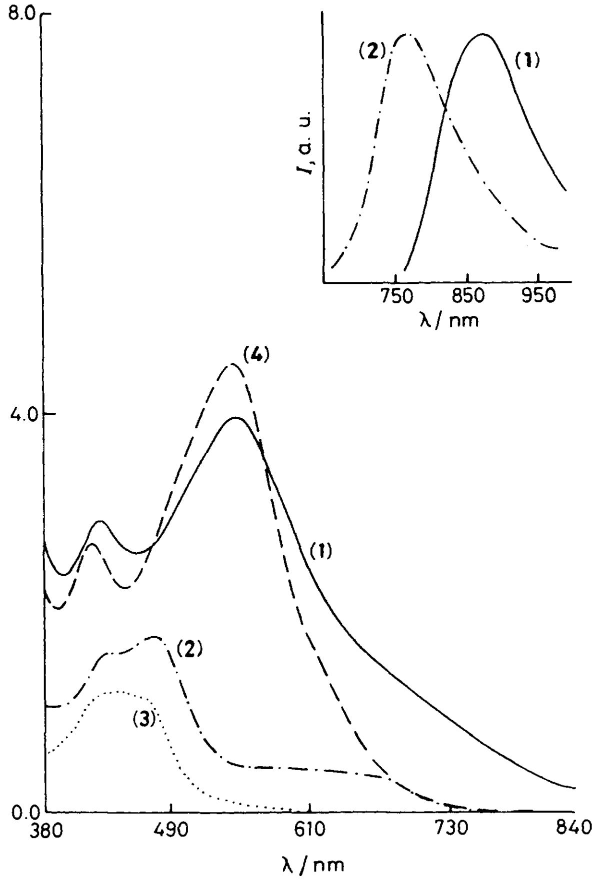

Figure 2. Absorption spectra for complexes (**1**)—(**4**) and (inset) emission spectra for complexes (**1**) and (**2**).

The absorption band of (**1**) with λ_{max} = 428 nm (Figure 2) corresponds to the Ru → bpy CT band at 430 nm of (**3**). The broad band with λ_{max} = 549 nm is contributed to by the Os → dpp and Ru → dpp CT transitions responsible for the bands of (**2**) at 475 nm and (**3**) at 470 nm, both strongly displaced to lower energies because in (**1**) dpp bridges two metal units. The high absorption tail of (**1**) towards the red can be attributed to triplet Os → dpp CT transitions.

The luminescent band of (**1**) (Figure 2 inset, Table 1), can be assigned to a triplet Os → dpp CT level, considerably red-shifted from that of (**2**) for the reason discussed above. This assignment is confirmed by the relatively short lifetime of the luminescence emission of (**1**) at 77 K, typical of Os^{II}–polypyridine complexes. Corrected excitation spectra at room temperature have shown that excitation in the Ru → bpy or Ru → dpp CT bands is followed by conversion to the luminescent level with the same efficiency as is excitation in the Os → dpp CT band.

The comparison of the properties of (**1**) and (**4**) is quite interesting. For both complexes, reduction first takes place on the dpp ligands, while oxidation first occurs in the central metal (Os) core for (**1**), and in the peripheral metals (Ru) for (**4**). The latter result as well as the comparison with the emission spectra of the parent $Ru(dpp)_3^{2+}$ and $Ru(bpy)_2(dpp)^{2+}$ complexes[5] show that the luminescence of (**4**) originates from the peripheral Ru-containing units. Thus, both (**1**) and (**4**) feature the so called 'antenna effect,'[6—8] but in opposite directions; in (**1**) luminescence takes place from the central chromophore, which receives the energy collected by the peripheral chromophores (concentration effect), whereas the reverse occurs in (**4**) (diffusion effect).

It is interesting to note that the excited state energy of the central Os-containing core should not be substantially affected on replacing the peripheral $Ru(bpy)_2^{2+}$ units with Ru(2,3-dpp)$_2^{2+}$. This could open the way to higher, luminescent oligomers.

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 Pubblica Istruzione, and NATO (Grant No. 937/86) for financial support.

Received, 10th May 1989; Com. 9/01965K

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