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LETTER

1,4,5,8-Tetraoxonaphthalene redox species in dinuclear ruthenium complexes: resonance Raman and electronic spectra

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Introduction

Dinuclear ruthenium complexes provide interesting examples for understanding the mechanism of electronic transfer between metal centers in mixed valence states [1–7]. Since the extent of the overlap between the metal centers is expected to depend on the mixing of the metal and bridging ligand orbitals, the use of non-innocent ligands may favor the formation of class III complexes [8–12].

Some of us recently have reported [13] the synthesis and the characterization of a series of ruthenium complexes of general formula $[Ru_2(bpy)_4tetrox]Y_n$ ($n=2$, 3, 4; $Y=ClO_4$, PF_6; tetrox = 1,4,5,8-tetraoxonaphthalene) which were postulated to contain dinuclear cations with the tetraoxolene acting as bis-bidentate bridging ligand towards two ruthenium–bis(2,2′-bipyridine) moieties. The choice of the tetrox ligand was suggested from the following considerations: (i) this ligand may potentially exist in five different oxidation states, as shown in Scheme 1; (ii) several reports on ruthenium dioxolene complexes evidenced the non-innocent nature of this kind of ligand toward ruthenium [14–18].

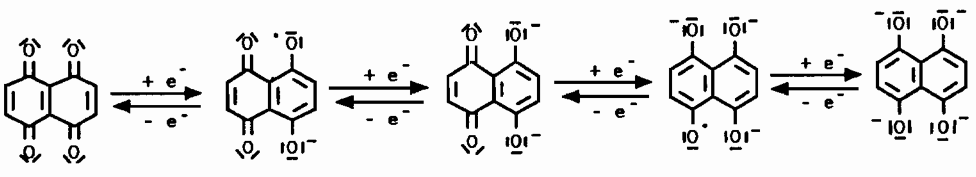
The dipositive derivative was described as containing two ruthenium(II) cations bridged by $tetrox^{2-}$ species and the tripositive cation $[Ru_2(bpy)_4tetrox]^{3+}$ was described as $Ru(III)(tetrox^{2-})Ru(II)$ on the basis of the electronic and EPR spectra. The latter spectra provided evidence that the molecular orbital containing the unpaired electron is mainly localized on the metal ion with a partial delocalization on the bridging ligand. The occurrence of delocalized structure is supported by the presence of a very intense absorption band in the electronic spectrum at very low energy (4800 cm^{-1}, $\epsilon = 9300$ $mmol^{-1}$ cm^2), which has been assigned to an intervalence transition.

The one electron oxidation product of this complex, i.e. $[Ru_2(bpy)_4tetrox]^{4+}$ is diamagnetic, with possible descriptions as either $[Ru(III)(tetrox^{2-})Ru(III)]^{4+}$ or $[Ru(II)(tetrox)Ru(II)]^{4+}$. The first description would require a strong antiferromagnetic interaction between the two $4d^5$ metal ions; the latter requires a neutral diquinone bridging the two $4d^6$ metal ions. The first hypothesis was believed to be less probable and therefore the latter formulation was suggested appropriate for describing the electronic structure of this compound.

In order to confirm the previous assignment, we have now performed a resonance Raman (RR) investigation on these compounds, which allow us also to assign their electronic spectra by comparison with those of thc $[Ru_2(py)_8(tetrox)]^{n+}$ chromophores, which have been synthesized for this purpose.

Results and discussion

Using the exciting lines at 457.9, 488 and 514.5 nm of an argon ion laser, we obtained Raman spectra of the three complexes in resonance and preresonance with the bands of the absorption spectra (Fig. 1), which can be assigned, as confirmed below, to charge transfer metal–bipyridine transitions. Using instead the exciting line at 632.8 nm of a helium–neon laser, we recorded Raman spectra in rcsonance and preresonance with the electronic bands which will be assigned below to the tetrox ligand.



Scheme 1.

0020-1693/91/$3.50

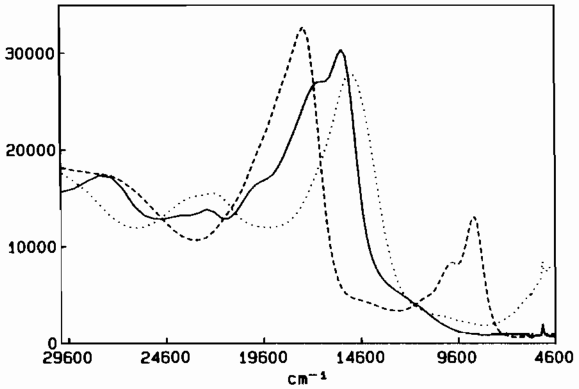


Fig. 1. Electronic spectra of $[Ru_2(bpy)_4(tetrox)]^{n+}$ in acetonitrile: $n=2$ (——), 3 (·····), 4 (– – –). The arrows indicate the laser frequencies used to excite the RR spectra.

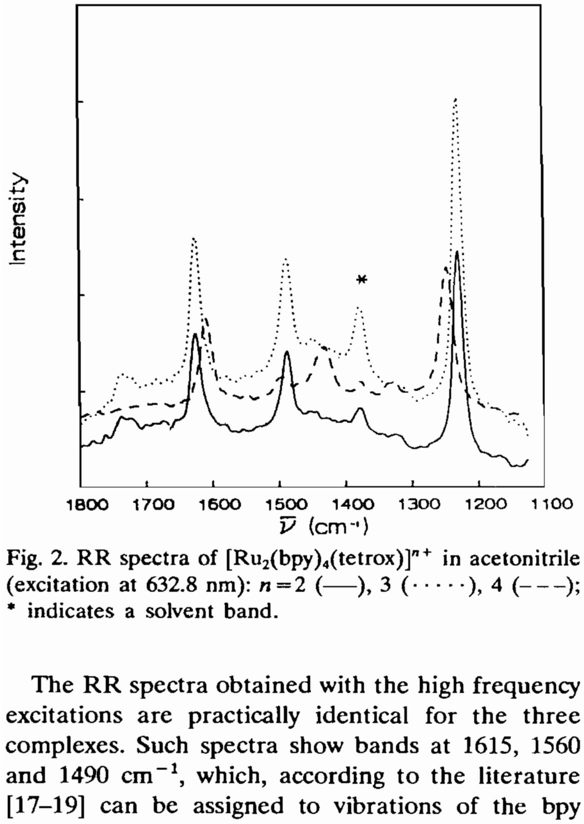


Fig. 2. RR spectra of $[Ru_2(bpy)_4(tetrox)]^{n+}$ in acetonitrile (excitation at 632.8 nm): $n=2$ (——), 3 (·····), 4 (– – –); * indicates a solvent band.

The RR spectra obtained with the high frequency excitations are practically identical for the three complexes. Such spectra show bands at 1615, 1560 and 1490 cm^{-1}, which, according to the literature [17–19] can be assigned to vibrations of the bpy ligand.

The RR spectra measured upon 632.8 nm excitation (Fig. 2) for $[Ru_2(bpy)_4(tetrox)]^{2+}$ and $[Ru_2(bpy)_4(tetrox)]^{3+}$ are practically identical to each other, while they are different from the RR spectrum of $[Ru_2(bpy)_4(tetrox)]^{4+}$.

The spectra of the two complexes in the lower oxidation states show strong bands at 1625, 1488 and 1230 cm^{-1}, which can be assigned to vibrations of the tetraoxolene ligand. In detail the band at 1625 cm^{-1} can be assigned to the C=O stretching mode, the band at 1488 cm^{-1} to a characteristic phenolate deformation mode and the band at 1230 cm^{-1} to a stretching mode of the aromatic rings [20] (this band, which exhibits the highest intensity, is observed also upon 457.9, 488 and 514.5 nm excitation, probably because of a preresonance effect with the electronic absorption of the tetrox ligand). Therefore, we can retain that the oxygenated ligand is in the same oxidation state both in $[Ru_2(bpy)_4(tetrox)]^{2+}$ and $[Ru_2(bpy)_4(tetrox)]^{3+}$.

The RR spectrum of $[Ru_2(bpy)_4(tetrox)]^{4+}$ shows instead the strongest bands at 1609, 1432 and 1249 cm^{-1} (the last one again observed also in the RR spectra of the same compound excited with the argon laser). This result confirms that, on passing from $[Ru_2(bpy)_4(tetrox)]^{3+}$ to $[Ru_2(bpy)_4(tetrox)]^{4+}$, the oxygenated ligand is modified. The shift toward lower frequencies (from 1625 to 1609 cm^{-1}) of the C=O stretching mode can be explained with an increase of π backbonding, while the disappearance of the 1488 cm^{-1} band, typical of phenolates, is in agreement with the oxidation of the tetrox ligand to diquinone.

The RR spectra, therefore, fully support the previous description of the three dinuclear complexes. One-electron oxidation of $(Ru(II)(tetrox^{2-})Ru(II))^{2+}$ removes the electron from the metal ion with only partial involvement of the ligand, while the second one-electron oxidation process leads to a larger rearrangement of the electron density, which now corresponds to $(Ru(II)(tetrox)Ru(II))^{4+}$.

These RR data allow us to suggest a partial assignment of the electronic spectra of the $[Ru_2(bpy)_4(tetrox)]^{n+}$ chromophores. For this purpose the complex $[Ru_2(py)_8(tetrox)](PF_6)_2$ has been synthesized. Cyclic voltammetry experiments in deaerated acetonitrile show that this compound exhibits three reversible monoelectronic redox processes at -1.28, 0.09 and 0.47 V versus the Fc^+/Fc couple. The redox behavior is the same as that observed for the bipyridine derivative (-1.25, 0.11 and 0.42 V versus Fc^+/Fc) [13].

The parameters of the electronic spectra of $[Ru_2(bpy)_4(tetrox)]^{n+}$ and $[Ru_2(py)_8(tetrox)]^{n+}$ are reported in Table 1. For the latter compound solutions containing the tripositive and the tetrapositive cations were obtained by exhaustive electrolysis at 0.25 and 0.7 V versus Fc^+/Fc of solutions of the dipositive derivative.

The RR spectra show that the absorptions of the dipositve and tripositive cations in the range 14 000–16 000 cm^{-1} correspond to internal transitions of the $tetrox^{2-}$ ligand. In the dipositive cations the metal is present as ruthenium(II) and only metal-to-ligand charge transfer (MLCT) transitions involving the d metal orbitals and the π^* orbitals of

TABLE 1. Electronic spectra of $[Ru_2(bpy)_4(tetrox)]^{n+}$ and $[Ru_2(py)_8(tetrox)]^{n+}$ complexes ($n=2$, 3, 4) in acetonitrile[a, b]

	$[Ru_2(bpy)_4tetrox]^{n+}$	$[Ru_2(py)_8tetrox]^{n+}$	Assignment
$n=2$	12900sh		LLCT[c]
	15400 (4.43)	14600 (4.50)	Int. tetrox
	16600 (4.35)	16000sh	Int. tetrox
	19400sh	17400sh	
	22200 (4.16)		Ru–π^*(1)bpy
	23400 (4.13)		Ru–π^*(1)bpy
		26000 (4.60)	Ru–π^*(1)py
	27400 (4.22)		Ru–π^*(2)bpy
	30000sh		
$n=3$	4800 (3.96)	<4600	IT Ru–Ru
	10500sh		LLCT[c]
	14800 (4.38)	13900 (4.30)	Int. tetrox
	21900 (4.21)		Ru–π^*(1)bpy
	22500sh		Ru–π^*(1)bpy
	28000sh		Ru–π^*(2)bpy
		28800 (4.31)	Ru–π^*(1)py
$n=4$	8700 (4.12)	8700 (3.77)	Ru–π^* tetrox
	9800 (3.75)	9600 (3.65)	Ru–π^*tetrox
	17300 (4.51)	17400 (4.35)	Int. tetrox
	26000 (4.22)		Ru–π^*(1)bpy

[a] In cm^{-1}; log ϵ in parentheses. [b] sh = shoulder. [c] See ref. 14.

the bpy and $tetrox^{2-}$ ligands are expected [21]. The observed bands shift to the blue on passing from the bipyridine derivative to the pyridine one and therefore are assigned to MLCT transitions. The proposed assignment is consistent with that reported by Lever and co-workers for similar chromophores [14–16].

The tripositive cations are mixed-valence complexes, since the metal is present as ruthenium(II) and ruthenium(III). The strong feature at 4800 cm^{-1} has been tentatively assigned to an intervalence transition involving the two metal ions. The same transition appears in the spectrum of the pyridine complex, but we were unable to determine its spectral parameters, because of the low sensitivity of our spectrophotometer in the IR region. We detect only a tail of a strong absorption, whose maximum falls lower than 4600 cm^{-1}. As for the spectra of the dipositive cations, MLCT transitions involving the ruthenium(II) orbitals and the π^* acceptor orbitals of the pyridine or bipyridine ligands are identified in the high energy side of the spectrum, in agreement with the RR results.

The band with maximum at c. 17 300 cm^{-1} in the spectrum of $[Ru_2(bpy)_4(tetrox)]^{4+}$ is assigned to an internal transition of $tetrox^0$ bridging ligand. This value must be compared to that of 19 500 cm^{-1} observed for the same absorption in the spectrum of the free diquinone ligand. The two bands at 8700 and 9800 cm^{-1} are not present in the spectrum of the free ligand and therefore must be charge transfer in character. We assign them to MLCT transitions involving the out-of-plane split d orbitals of the metal ions and the π^* LUMO of the diquinone ligand. Again, as supported by the RR spectra, the band occurring at 26 000 cm^{-1} in the spectrum of the $[Ru_2(bpy)_4(tetrox)]^{4+}$ chromophore must be attributed to the MLCT transition Ru–π^*(1)(bpy), shifting to higher energy on increasing the ionic charge of the chromophore.

Experimental

Materials

The $[Ru_2(bpy)_4tetrox](PF_6)_n$ complexes ($n=2$, 3, 4) were synthesized as previously described [13]. The complex $[Ru_2(py)_8(tetrox)](PF_6)_2$ was obtained following a similar procedure by using $Ru(py)_4Cl_2$ as reactant. *Anal.* Found: C, 44.29; H, 3.51; N, 8.12. Calc. for $C_{50}H_{48}F_{12}N_8O_6P_2Ru_2$: C, 44.51; H, 3.58; N, 8.31%.

Physical measurements

Resonance Raman spectra were measured on acetonitrile solutions of the samples by Coderg PHO and multichannel JASCO TRS-300 spectrophotometers using the lines at 457.9 (21 839 cm^{-1}), 488 (20 492 cm^{-1}) and 514.5 (19 436 cm^{-1}) nm of an argon ion laser and the line at 632.8 nm (15 803 cm^{-1}) of a helium–neon laser. Cyclic voltammograms and electronic spectra were obtained as previously described [22].

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