Inorganica Chimica Acta, 210 (1993) 159-165

Reinvestigation of the visible absorption bands of the 2,2'-bipyrimidine complexes $W(CO)_4(bpym)$ and (μ-bpym)$[M(CO)_4]_2$ (M = Mo, W) with resonance Raman spectroscopy; the emission spectrum of (μ-bpym)$[Mo(CO)_4]_2$

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(Received February 5, 1993)

Abstract

The character of the two lowest energy transitions of $W(CO)_4(bpym)$ and (μ-bpym)$[M(CO)_4]_2$ (M = Mo, W) were established with resonance Raman spectroscopy. According to these spectra the two bands belong to MLCT transitions to different π^* orbitals of the bpym ligand. Contrary to expectations it is not the first (lowest energy) but the second and more intense electronic transition which, according to the resonance Raman spectra, is directed to the lowest lying π^* orbital (b_{2u}^*, LUMO) of these complexes. This interpretation explains the different band intensities and the untypically low g values of the ESR signals of corresponding anion radicals. Excitation of (μ-bpym)$[Mo(CO)_4]_2$ in CH_2Cl_2 at 400 nm produced a weak emission with an onset at 700 nm. According to the excitation spectrum, this emission originates from the lowest MLCT-excited state of the complex.

Introduction

2,2'-Bipyrimidine (bpym) is a very peculiar bis(α-diimine) ligand, capable of bridging two metal complex fragments at a metal–metal distance of about 550 ppm in a D_{2h}-symmetric arrangement [1-3]. Bpym possesses three low-lying unoccupied molecular orbitals π^*_{1-3} [4, 5] for interaction with electron rich metals (Fig. 1). The LUMO (π^*_1) has b_{2u} symmetry and rather small MO coefficients at the four equivalent coordination centres, its nodal properties resemble that of the LUMO of 2,2'-bipyridine or biphenyl. The other two low-lying unoccupied MOs, a_u^* and b_{3g}^*, result from energetically equivalent combinations of π^*_{as} orbitals of the individual aromatic six-membered rings, leading to α-diimine coordination centres with χ, χ (a_u) and Ψ, Ψ (b_{3g}) character in Orgel's notation [6] (Fig. 2). The LUMO (b_{2u}^*) has Ψ, Ψ character which allows ligand mediated d–d interaction (Fig. 3).

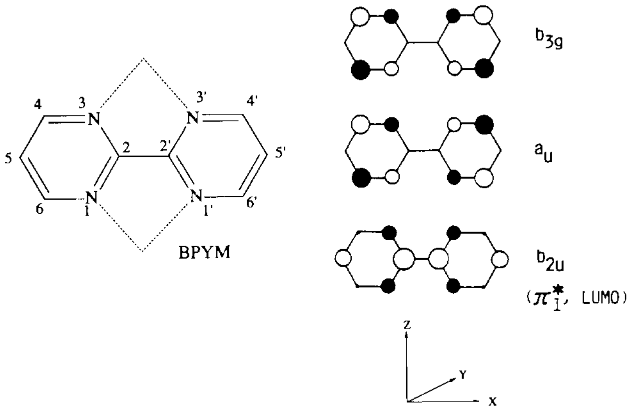

Fig. 1. Low-lying unoccupied π molecular orbitals of 2,2'-bipyrimidine.

Several homo- and heterodinuclear complexes of bpym with low-valent d^6- and d^{10}- configurated metal

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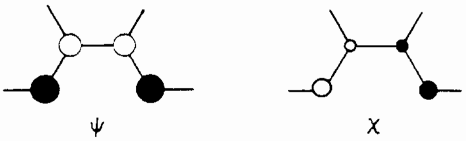

Fig. 2. Orgel's designation of π^* orbitals of α-diimine chelate ligands.

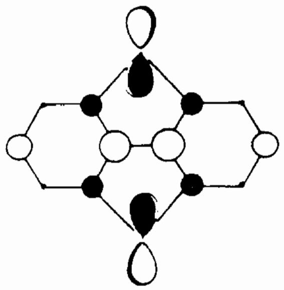

Fig. 3. b_{2u} (bpym)-mediated overlap of metal d-orbitals.

centres have been reported and studied with respect to their photo- and electrochemical properties [3–5, 7–13]. In contrast to homodinuclear complexes with coordinated fragments *fac*-$Re(CO)_3(Hal)$ [7] (*cis*/*trans* isomerism [8, 9]), *cis*-$^{2+}[Ru(N^\frown N)_2]$ [10] (*meso*/*rac* isomerism [11, 12]) and $^{+}[Cu(PPh_3)_2]$ (intramolecular distortion [3]), the dinuclear complexes (μ-bpym)$[M(CO)_4]_2$ (M = Mo, W [4, 13–16]) should be approximately D_{2h}-symmetric. Electronic spectra of these complexes have been reported and studied with respect to their pronounced solvatochromism [14–16]; three separate absorption bands can be distinguished in less polar solvents [4, 5, 15, 17]. Two solvatochromic bands in the visible region were attributed to allowed, z-polarized metal-to-ligand charge transfer (MLCT) transitions: from the antisymmetric d_{yz} combination to π^*_1 ($b_{3g} \rightarrow b_{2u}^*$), and from the symmetric d_{xy} combination to π^*_2 ($b_{1g} \rightarrow a_u^*$) [15]. A third intense band in the near-UV region is solvent insensitive [4, 13, 15] and has been attributed to a ligand-field (LF) transition with a rather large extinction coefficient because of partial MLCT character [13]. This band could also result from a z-polarized transition $b_{2u} \rightarrow b_{3g}^*(\pi^*_3)$ which would be allowed in the case of spectroscopically effective D_{2h} symmetry because of metal–metal interaction. Dodsworth and Lever have given a detailed description of this alternative and argued for effective C_{2v} symmetry at electronically rather isolated [16] metal/α-diimine chelate sites [15].

While there is clear evidence from ESR [18] and UV–Vis spectroelectrochemistry [19] for the b_{2u} character of the singly occupied MO in the anion radical complex $\{(\mu\text{-bpym})[Mo(CO)_4]_2\}^-$, the unusually small g factors of such paramagnetic species suggest the existence of rather close-lying excited states [18]. In this paper we present results from resonance Raman (rR) studies of complexes $W(CO)_4$(bpym) and (μ-bpym)$[M(CO)_4]_2$ (M = Mo, W) and of the reduced form of the mononuclear complex. Tetracarbonylmetal complexes of α-diimines are quite suitable for rR investigations as has been demonstrated for a number of mononuclear systems [20, 21]. In addition, we present evidence that the complex (μ-bpym)$[Mo(CO)_4]_2$ emits from its lowest excited state. Some mononuclear tetracarbonylmetal complexes show emission [21, 22], but dinuclear $M(CO)_4$ complexes of bis(α-diimine) ligands are not known to emit although several related dinuclear species do show luminescence [23, 24]. From the homodinuclear bpym complexes, the $Re(CO)_3Cl$ dimer does not emit [7] and the $^{2+}[Ru(bpy)_2]$ system only very weakly [10]; the $^{+}[Cu(PPh_3)_2]$ dimer is a special case since it adopts a strongly distorted 'entatic' conformation in the solid which might enhance luminescence intensity [3].

Experimental

Materials

The complexes were prepared according to previously published procedures [4, 13, 14]. All spectroscopic samples were prepared by standard inert gas techniques.

Instrumentation

UV–Vis absorption spectra were recorded on Perkin-Elmer Lambda 5 and Hewlett-Packard model 8450 A diode-array spectrophotometers. Resonance Raman spectra of solutions of the complexes in CH_3CN were obtained by excitation with the lines of an SP 2016 Ar^+ laser or by a CR-590 dye laser employing Coumarine 6 or Rhodamine 6G dyes pumped by the Ar^+ laser. The spectra were recorded by a Dilor XY spectrometer. Resonance Raman spectra of the reduction product of complex **I** ($\mathbf{I}^-$) were obtained by employing an IR-OTTLE cell [25] equipped with a Pt-minigrid working electrode and NaCl windows. The controlled-potential electrolysis of **I** within the OTTLE cell was carried out by using a PAR model 173 potentiostat.

Emission and excitation spectra were obtained on a SLM Instruments model 8000/8000S dual-monochromator spectrometer, which incorporates a photomultiplier-based photon-counting detector. A red-sensitive Hamamatsu R928 photomultiplier tube was used in these measurements. Excitation spectra were determined from samples that were optically dilute ($A < 0.1$) throughout the spectral region scanned and were corrected for wavelength variations in exciting-lamp intensity. In all these emission experiments the sample solutions were filtered through 0.22 μm millipore filters and then deoxygenated by N_2-purging for 15 min prior to taking measurements. IR and UV–Vis spectra were checked before and after irradiation to monitor possible sample degradation.

Emission lifetimes were recorded on a PRA system 3000 time-correlated pulsed single-photon-counting spectrometer. Samples were excited with light from a N_2-filled PRA model 510 flash lamp and the emission was detected with a thermoelectrically cooled red-sensitive Hamamatsu R955 photomultiplier tube. The resultant proton counts were stored on a Tracor Northern model 7200 microprocessor-based multi-channel analyzer. Subsequently the instrument response function was deconvoluted from the luminescence data and fitted by an iterative least-squares procedure. The reported lifetimes represent an average of at least three readings.

Low temperature emission lifetime measurements were performed with an Oxford Instruments DN1704K liquid-N_2 cooled variable-temperature cryostat fitted with synthetic sapphire inner windows and quartz outer windows. Samples were contained in a fused-quartz 1 cm path length square cell and were rigorously deaerated by successive freeze–pump–thaw cycles. The temperature in the cell was maintained to ±0.2 K.

Results and discussion

Resonance Raman spectra

The rR spectra of $W(CO)_4(bpym)$ (**I**) and (μ-bpym)$[W(CO)_4]_2$ (**II**) are presented in Figs. 4 and 5, respectively, together with the absorption spectra as an insert. Because of the restricted wavelength region of the laser source, rR spectra of **I** could only be measured in resonance with the lowest-energy band. For complex **II** both absorption bands could partly be covered by the laser lines and the resulting rR spectra could therefore be used to assign and characterize the electronic transitions of this complex.

For both compounds the main rR effects are observed for bands in the 1000–1600 cm^{-1} region. Their wavenumbers are collected in Table 1 together with those of the Mo complex (μ-bpym)$[Mo(CO)_4]_2$ (**III**) and of $Ru(bpym)_3^{2+}$. The most obvious difference between the spectra of **I** and **II** or **III** is the occurrence of less Raman bands for complexes **II** and **III**. This effect is caused by the difference in symmetry of the two complexes. In complexes **II** and **III** the bpym molecule has retained its D_{2h} symmetry and only totally symmetric (A_g) vibrations are observed in the rR spectra just as for the free ligand [27]. When the symmetry is lowered to C_{2v} in **I**, the A_g vibrations transform into Raman active A_1 modes. In addition, A_1 vibrations are derived from the Raman forbidden B_{2u} modes of the ligand having D_{2h} symmetry. This explains the observation of more Raman bands for **I** and $Ru(bpym)_3^{2+}$ than for **II**, **III** and free bpym. Instead of a single Raman band for **II**, two highest frequency ligand vibrations are observed for **I** at 1548 and 1577 cm^{-1}, respectively. In addition two extra bands show up in the spectra of **I** at 1198 and 1417 cm^{-1}, not present in the spectra of **II** and bpym.

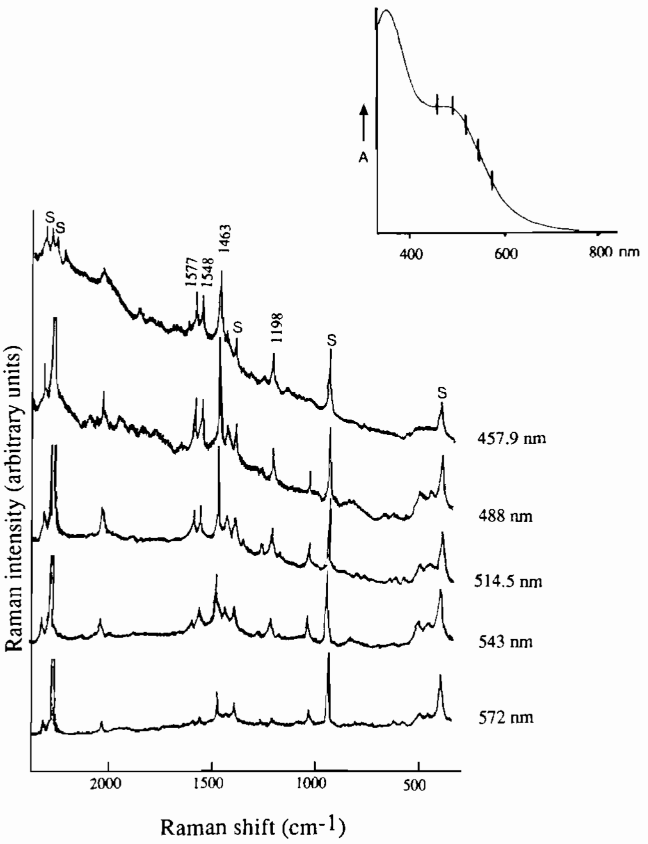

Fig. 4. Resonance Raman spectra of $W(CO)_4(bpym)$ in acetonitrile solution. Excitation wavelength from top to bottom: 458, 488, 514.5, 543 and 572 nm (absorption spectrum and excitation wavelengths in the insert, top right). S: solvent band.

All rR bands in the 1000–1600 cm^{-1} region belong to vibrations of the bpym ligand, which means that the electronic transitions are located at or directed to this ligand. Since internal transitions of bpym occur at much higher energy, these rR effects will be caused by excitation into metal-to-bpym charge transfer (MLCT) transitions. The MLCT character of the transitions is supported by the observation of a resonance enhanced CO vibration at about 2000 cm^{-1} for **I** and **II** and of bands at 482 and 434 cm^{-1} in the spectra of complex **I** belonging to symmetrical metal–carbon stretching modes of the $W(CO)_4$ moiety.

It is noteworthy that a different set of Raman bands is resonance enhanced upon excitation into either of the two absorption bands of **II** (Fig. 5). Apparently, different bonds of bpym are affected by these transitions, which will therefore be directed to different π^* orbitals of this ligand. However, from these spectra alone it

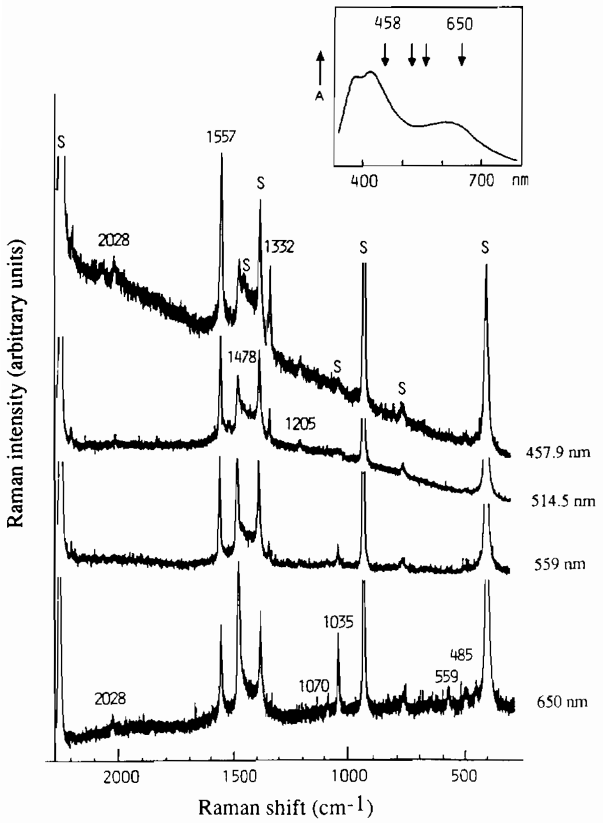

Fig. 5. Resonance Raman spectra of (μ-bpym)[W(CO)$_4$]$_2$ in acetonitrile solution. Excitation wavelength from top to bottom: 458, 514.5, 559 and 650 nm (absorption spectrum and excitation wavelengths in the insert, top right). S: solvent band.

TABLE 1. Vibrational frequencies (cm^{-1}) of 2,2′-bipyrimidine and several of its complexes from (resonance) Raman spectra

bpym[a]	(bpym)[M(CO)$_4$]$_2$[a]		W(CO)$_4$-(bpym)[a]	Ru-(bpym)$_3^{2+}$ [c]
	M=Mo	M=W		
			1577	1585
1573(s)	1556	1557	1548	1558
1455(m)	1469	1478	1463	1479
	[b]	[b]	1417	1414
1338(w)	1332	1332	1335	1339
	1205	1205	1198	1207
				1120
1077(w)		1080		1070
998(m)	1031	1035	1017	1028
748(w)				

[a] Spectra recorded for solutions in acetonitrile. [b] Spectral region obscured by solvent bands. [c] Spectrum recorded for an aqueous solution of Ru(bpym)$_3$Cl$_2$ [26].

cannot be decided which of the π^* orbitals of bpym in Fig. 1 are involved in the separate transitions.

We have therefore tried to establish the character of the LUMO of complexes **I** and **II** by measuring the rR spectra of their reduced species. Unfortunately, reduction of **II** afforded very poor rR spectra. However, the reduction product (**I**$^-$) of **I** gave reliable rR spectra. One of these spectra is shown in Fig. 6 together with the absorption spectrum of **I**$^-$ as an insert. The resonance enhanced Raman bands are collected in Table 2 together with those of **I** and of Ru(bpym)$_3^{2+}$ in its ground and lowest excited state.

The absorption spectrum of **I**$^-$ (insert Fig. 6) closely resembles that of bpym$^-$ [19]. Both spectra show a band around 500 nm with the vibrational structure

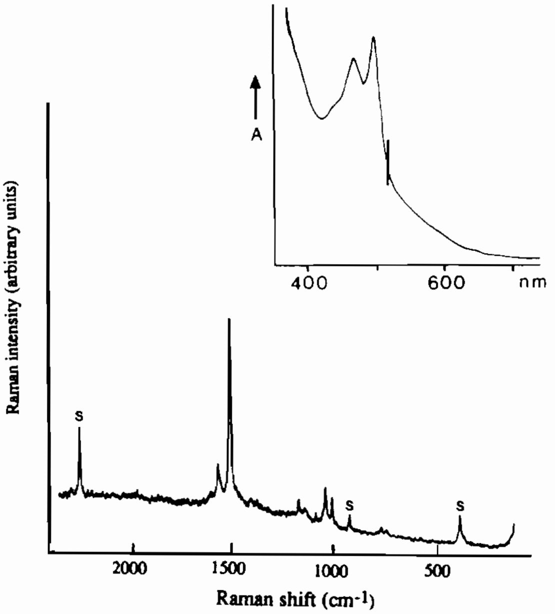

Fig. 6. Resonance Raman spectrum of [W(CO)$_4$(bpym)]$^-$ (**I**$^-$) in acetonitrile solution. Spectrum recorded for the complex ion in an OTTLE cell and excited with 514.5 nm (absorption spectrum and excitation wavelength in the insert, top right). S: solvent band.

TABLE 2. Raman frequencies (cm^{-1}) of coordinated 2,2′-bipyrimidine in two complexes, in a reduced species and in an excited state

W(CO)$_4$-(bpym)[a]	[W(CO)$_4$-(bpym)]$^-$ [a]	Ru-(bpym)$_3^{2+}$ [b]	Ru(bpym)$_3^{2+*}$ [b]	
			440 nm	355 nm
1577	1570	1585		1560
1548	1511	1558	1530	1530
1463		1479		
1417		1414		
1335		1339		1362
				1255
1198	1172	1207	1182	1180
		1120		
	1040	1070	1038	1042
1017	1007	1028	1014	1018

[a] Spectra recorded for the complex and its reduced form in acetonitrile. [b] Spectra recorded for the complex ion in its ground and excited state from aqueous solutions of Ru(bpym)$_3$Cl$_2$ [26].

characteristic for a $\pi \rightarrow \pi^*$ transition. The intraligand character of this transition is also evident from the rR spectra of I^- which do not show resonance enhancement of Raman intensity for any CO-stretching mode of the $W(CO)_4$ moiety.

For the assignment of the absorption spectra it is of importance to note that coordination of a second $W(CO)_4$ fragment to the bpym ligand of **I**, giving rise to the formation of **II**, is accompanied by a shift of the MLCT bands to lower energies. Because of this both bands of **II** could be covered by the available laser lines, whereas only the first absorption band of **I** could be studied with rR spectroscopy.

Excitation into either of the two bands of **II** gave rise to very different rR effects (Fig. 5). Excitation into the first band with 650 nm was accompanied by rR effects for bands at 1035, 1478 and 1557 cm^{-1}. Going to shorter wavelength, the 1035 and 1478 cm^{-1} bands disappeared while the 1557 cm^{-1} band increased in intensity and a new band appeared at 1332 cm^{-1}. The latter band is apparently only in resonance with the second electronic transition.

Interpretation of these rR effects in terms of bond order changes is not an easy task since most stretching modes of bpym are highly mixed ring deformations [27]. Yet, especially the rR effect observed for the 1332 cm^{-1} band gives valuable information about the electronic transitions of complex **II**.

Normal coordinate analyses of biphenyl [28], 2,2′-bipyridine (bpy) [29], bpym [27] and $Ru(bpy)_3^{2+}$ [30] have shown that the symmetric vibration at about 1300 cm^{-1} has a large contribution from the inter-ring C–C bond. Takahashi and Maeda observed that reduction of biphenyl gave rise to a frequency increase of this inter-ring vibration from 1287 to 1326 cm^{-1} [31]. They ascribed this effect to an increase of bond order of the central C–C bond upon occupation of the LUMO of this molecule. This interpretation was later confirmed by the results from molecular orbital calculations [32].

More recently, similar frequency shifts have been observed for complexes of bpy upon reduction [33–35] or by going to the lowest MLCT state [36–39]. Thus, the inter-ring stretching vibration shifted from 1285 to 1357 cm^{-1} upon reduction of bpy [34] and from 1317 to 1363 cm^{-1} upon excitation of $Ru(bpy)_3^{2+}$ to its lowest MLCT state [38]. Reduction of all bpy ligands in $Ru(bpy)_3^{2+}$ to give $Ru(bpy)_3^{1-}$ again caused a shift of this vibration from 1320 to 1358 cm^{-1} [33]. Reduction of one bpy ligand in $Fe(bpy)_3^{2+}$ to give $Fe(bpy)_3^{+}$ gave rise to the appearance of a new Raman band at 1360 cm^{-1} [34]. Caswell and Spiro studied the rR spectra of $Ru(NH_3)_5(4,4\text{-bpy})^{2+}$ in its ground and excited state and again observed a frequency increase of the inter-ring stretching mode from 1300 to 1339 cm^{-1} [40]. Finally, Cooper and Wertz studied the electronic absorption and rR spectra of the three complexes $Ru(bpy)_2(CN)_2^{n-}$ ($n=0$, 1, 2) and measured a shift of the inter-ring stretch from 1317 to 1351 cm^{-1} upon going from $n=0$ to $n=1$ and 2 [35].

In all these cases, the frequency increase has been ascribed to the quinonoid structure of the LUMO populated either by reduction or by MLCT excitation. The b_{2u}^* orbital of bpym has a similar quinonoid structure (Fig. 1) and occupation of this orbital will also be accompanied by a strengthening of the inter-ring C–C bond causing a shift of the corresponding vibration to higher frequency. This has indeed been established for $Ru(bpym)_3^{2+}$ which showed a frequency increase for this vibration from 1336 to 1362 cm^{-1} upon going from the ground state to the lowest excited state [26] (Table 2). Unfortunately, this 1362 cm^{-1} band was not resonance enhanced by the electronic transition of $Ru(bpym)_3^{2+*}$ in the visible region, but only showed up upon excitation with the 354.7 nm laser line. Since we could only excite the rR spectra of I^- with visible laser lines no Raman band around 1360 cm^{-1} was expected and indeed observed for this radical anion. There is, however, a close agreement between the rR spectra of I^- and $Ru(bpym)_3^{2+*}$ upon visible excitation (Table 2) and a similar correspondence is therefore expected for the UV-excited rR spectra of both complex ions. The above results show that in both the reduced species and lowest MLCT states of bpy as well as of bpym complexes the same π^* orbital is occupied in which the inter-ring C–C bond is strengthened. In the case of bpym this orbital is the proposed LUMO of Fig. 1 having b_{2u}^* symmetry.

Similarly, excitation of these complexes into an MLCT transition directed to this orbital is expected to be accompanied by a rather strong rR effect for the inter-ring stretching mode. However, the rR spectra of **II** show the remarkable effect that this vibration *is not resonance enhanced by the first transition but by the second one*. This observation can only lead to the conclusion that this second absorption band belongs to the z-polarized transition to the LUMO ($b_{3g} \rightarrow b_{2u}^*$). If this assignment is correct, the first absorption band must belong to the z-polarized transition to the SLUMO ($b_{1g} \rightarrow a_u^*$). Indeed, occupation of a_u^* will hardly affect the inter-ring bond (Fig. 1) and therefore not be accompanied by an rR effect for the inter-ring stretch.

This new result contrasts with the assignment of Dodsworth and Lever [15] which was for obvious reasons based on the well established ordering of the virtual orbitals of 2,2′-bipyrimidine. The new assignment does, however, agree with the relative intensities of the two absorption bands since the $b_{3g} \rightarrow b_{2u}^*$ transition, taking place between strongly interacting orbitals, will be more intense.

The situation is less clear for complex I since Raman excitation of this compound could only take place into its first absorption band. In agreement with complex **II** these rR spectra did not show any rR effect for a band at about 1300 cm^{-1} (Fig. 5). In contrast to complex **I**, the complex ion $Ru(bpym)_3^{2+}$ has been excited with 441.6 and 363.8 nm into both the first and second absorption band [26]. In this case resonance enhancement of Raman intensity was observed for the inter-ring stretch at 1339 cm^{-1} but again only upon excitation with 363.8 nm into the second absorption band. This suggests that also for the mononuclear bpym complexes the second electronic transition takes place to the LUMO, the first one to the SLUMO.

Apart from the 1300 cm^{-1} band, the complexes **I**, **II** and $Ru(bpym)_3^{2+}$ [26] have in common that their highest frequency ligand vibrations (1573 and 1548 cm^{-1} for **I**, 1557 cm^{-1} for **II**, 1585 and 1558 cm^{-1} for $Ru(bpym)_3^{2+}$) increase in intensity upon going to the second electronic transition. This effect is again connected with the quinonoid structure of the LUMO of bpym which involves a weakening of the C(2)–N(1), C(2)–N(3), C(4)–C(5) and C(5)–C(6) bonds (Fig. 1) with respect to the ground state. The two highest frequency modes of bpym [27] and bpy [29] have their largest displacements along these bonds and they will therefore be strongly affected by occupation of this orbital. Indeed, these vibrations shift to lower frequencies upon excitation of $Ru(bpym)_3^{2+}$ to its MLCT state and upon reduction of complex **I** (Table 2). The increasing rR effects of these high-frequency vibrations upon going to shorter wavelength excitation of **I**, **II** and $Ru(bpym)_3^{2+}$ again demonstrate that the second electronic transition of these complexes is directed to the LUMO of bpym and not the first low-energy transition.

Emission spectra

The ligand bpym shows a strong emission at 419 nm upon excitation at 330 nm. Upon irradiation with 400 nm, long-wavelength emission was observed for the complex (μ-bpym)$[Mo(CO)_4]_2$ (**III**) in CH_2Cl_2 with an onset at the foot of the first absorption band (*c*. 700 nm, Fig. 7). The maximum of the emission was outside the detection region of the spectrophotometer. The emission appeared to be quite short-lived with $\tau < 3$ ns at 283 K and 8 ns at 80 K in EPA.

Maxima of a corrected excitation spectrum (emission monitored at 750 nm) for **III** were found at 625, 445 and 390 nm, close to the absorption maxima of the complex in this solvent (672, 442 and 390 nm). The emission thus clearly originates from the lowest energy MLCT state; a similar situation for long-wavelength absorbing dinuclear complexes was found for heterocycle-bridged bis(pentacarbonyltungsten) species [41].

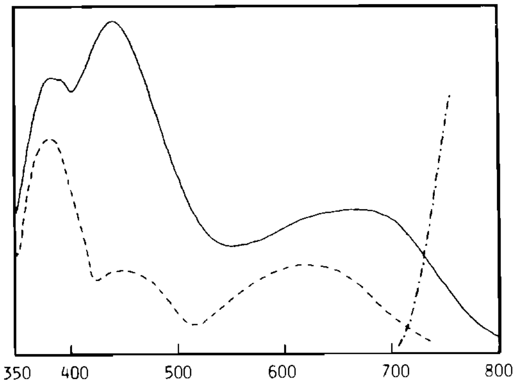

Fig. 7. Absorption (——), emission (–··–) and excitation (– – –) spectrum of (μ-bpym)$[Mo(CO)_4]_2$ in dichloromethane solution at 283 K. Emission after 400 nm excitation, excitation spectrum monitored at 750 nm.

The intensity difference at about 450 nm between absorption and excitation spectra could indicate the presence of an additional non-radiative process, possibly via a close-lying ligand-field state.

Conclusions

The rR data of complexes **I**–**III** lead to the remarkable conclusion that the first (low-energy) band of these complexes belongs to an MLCT transition to the SLUMO (a_u*) and the second band to a transition to the LUMO of bpym. While such an interpretation helps to explain the different band intensities and the unusually small *g* factors of the ESR signals of corresponding radical anion species [18], this result becomes even more remarkable when it is realized that not only the LUMO of these complexes has $b_{2(u)}$* character, but that also, at least in the case of $Ru(bpym)_3^{2+*}$ [26], the same LUMO is occupied in the lowest MLCT-excited state. This can only agree with the above mentioned reversed order of electronic transitions if the relaxation in the respective MLCT states ($b_{3g} \rightarrow b_{2u}$* and $b_{1g} \rightarrow a_u$* for **II** and **III**) is very different. Such an effect would be quite uncommon and, although the rR data are evident and the conclusions rather straightforward, further proof for this reassignment of the electronic transitions is certainly necessary.

Acknowledgements

Dr F. Hartl is thanked for recording the resonance Raman spectra of the complex ion $[W(CO)_4(bpym)]^-$ in his newly developed OTTLE cell.

This work was supported by grants from the Netherlands Foundation for Chemical Research (SON), the

Netherlands Organization for the Advancement of Pure Research (NWO), the Deutsche Forschungsgemeinschaft (DFG), the Petroleum Research Fund (USA) and by a fellowship (M.M.Z.) of the CSIR (South Africa).

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