The Electronic Absorption Spectrum and Structure of the Emitting State of the Tris(2,2′-bipyridyl)ruthenium(II) Complex Ion

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The directly determined absorption spectrum (250—650 nm) of the optically excited species $^{*}[Ru(bipy)_3]^{2+}$ (bipy = 2,2′-bipyridyl) is presented and assigned. The promoted (metal to ligand charge transfer) electron is localised on one of the three bipy ligands, as in the formulation $[Ru^{III}(bipy)_2(bipy^-)]^{2+}$, while the known emission photoselection data imply that the promoted electron resides on the same ligand throughout.

It was for many years customary to assume that in the thermally equilibrated (emitting) excited states, (1*), of $[Ru(bipy)_3]^{2+}$ (1) (bipy = 2,2′-bipyridyl), an electron was transferred from the metal core to an acceptor orbital delocalised over all three ligands.[1,2] This view is now becoming untenable. Raman studies have indicated that (1*) contained an identifiable $bipy^-$ ligand [3,4] while e.s.r.[5] and u.v.–visible [6] spectroscopy have led to the same conclusion for $(1)^-$, which we formulated as $[Ru^{II}(bipy)_2(bipy^-)]^+$. It remained, however, to demonstrate unequivocally the *simultaneous* presence of bipy together with $bipy^-$ as distinct ligands in (1*), as we had done for $(1)^-$. This feat has recently been accomplished by Woodruff and co-workers [7] for the Raman spectrum of (1*). We have independently approached the problem by examination of the u.v.-visible absorption spectrum of (1*), reasoning that, as in $(1)^-$, bands diagnostic of separate bipy and $bipy^-$ chromophores should be evident. We find this is indeed the case, but understates the richness and complexity of the spectrum.

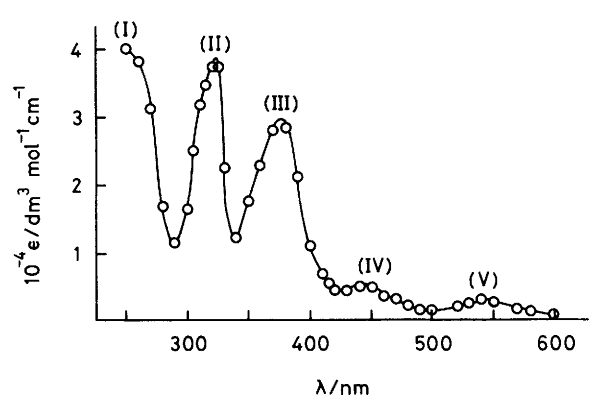

Figure. The absorption spectrum of $^{*}[Ru(bipy)_3]^{2+}$ in water at room temperature

Results and Discussion

Previous reports [2,8] of the spectrum of (1*) are incomplete in the visible region, and differ among themselves both in the shape of the bands and the reported absorption coefficients. Our own results (Figure) agree fully with the data of Lachish *et al.*,[8a] and confirm details discernible therein but absent in other published spectra. The present studies extend through the visible region down to 650 nm, and we have discovered at least one hitherto unsuspected absorption. In addition, further spectro-electrochemical investigations of Group 8 bipy complexes [9] have enlarged the range of suitable model compounds. As a result, we can now offer a detailed assignment (Table) according to the localised charge-transfer formulation, $[Ru^{III}(bipy)_2(bipy^-)]^{2+}$, for (1*). A semi-quantitative test of these assignments is then provided by comparison of absorption coefficients (corrected as necessary for the number of chromophores); we find satisfactory agreement in each case.

Band (I) (40 000 cm^{-1}; ε = 40 000 $dm^3\,mol^{-1}\,cm^{-1}$).—This band is assigned to the overlapping $\pi(6) \longrightarrow \pi(8,9)$ bands of bipy and $bipy^-$, which we do not expect to be able to resolve separately.

Band (II) (31 250 cm^{-1}; ε = 37 000 $dm^3\,mol^{-1}\,cm^{-1}$).—This band is assigned to $\pi(6) \longrightarrow \pi^{*}(7)$ of co-ordinated bipy, giving an absorption coefficient per bipy ligand of 18 500 $dm^3\,mol^{-1}\,cm^{-1}$, as against 15 000 for $[Ir(bipy)_3]^{3+}$. The corresponding band in (1) itself is anomalously intense, because of interaction between ligand excitations and higher energy $[d \longrightarrow \pi(8)]$ metal to ligand charge-transfer (m.l.c.t.) transitions.[10,11] Thus the intensity *loss* in this region, on going from (1) to (1*), is due to the loss of the $Ru^{II}(bipy)$ chromophores as well as of one bipy function.

Band (III) (26 600 cm^{-1}; ε = 29 000 $dm^3\,mol^{-1}\,cm^{-1}$).—This band raises interesting issues. It is assignable largely to $bipy^-$ [more specifically, to $\pi(6) \longrightarrow \pi(7)$ of co-ordinated $bipy^-$], a proposal made early by Balzani and co-workers [12] but subsequently abandoned.[13] It is far too intense, however, for this alone to be a satisfactory assignment, and shows evidence of a high-energy shoulder, also discernible in the spectrum presented by Lachish *et al.*[8a] We had some difficulty in assigning the extra component. Neither $bipy^-$ nor $[Ru^{III}(bipy)_3]^{3+}$, $(1)^+$, shows any similar transition. The lowest $[\pi(6) \longrightarrow Ru^{III}]$ ligand to metal charge-transfer (l.m.c.t.) transition of (1^+) is at 14 700 cm^{-1} and is much too weak (ε = *ca.* 600), as is the band in (1^+) at 24 100 cm^{-1} (ε = 3 400),[9,14] which we suspect of contributing to band (IV), below. Nor is the band a property of $bipy^-$–M^{III} systems in general, since it is absent in $[Al(bipy^-)_3]$.[15] We must therefore look for a transition,

Table. Proposed assignments for $^*[Ru(bipy)_3]^{2+}$, with data for model systems

					Model bands [c]		
Band [a]	ν/cm^{-1}	ε [b]/dm^3 mol^{-1} cm^{-1}		Species	ν/cm^{-1}	ε/dm^3 mol^{-1} cm^{-1} per relevant ligand	Remarks
(I)	40 000	40 000	$\pi(6) \longrightarrow \pi(8,9)$ of both bipy and bipy$^-$	$[Ru(bipy)_3]^{3+}$	42 900	11 000	
				$[Ir(bipy)_3]^{3+}$	40 000	20 000	
				$[Al(bipy^-)_3]$	37 700	5 400	*d*
				$Na(bipy^-)$	38 500	6 000	*e*
(II)	31 250	37 000	$\pi(6) \longrightarrow \pi(7)$ of bipy	$[Ru(bipy)_3]^{2+}$	35 100	<23 000	[$+d \longrightarrow \pi(7)$; see text]
				$[Ru(bipy)_3]^{3+}$	32 900	11 000	
				$[Ir(bipy)_3]^{3+}$	32 100	15 000	
(III)	26 600	29 000	$\pi(6) \longrightarrow \pi(7)$ of bipy$^-$ + l.m.c.t. ($\pi \longrightarrow$?)	$[Ru^{II}(bipy^-)_3]^-$	29 800	12 000	*f*
				$[Ru^{II}(bipy^-)_2(bipy)]$	29 000	14 300	*f*
				$[Ir^{III}(bipy^-)_3]$	25 400	8 000	bipy$^-$ $\pi(6) \longrightarrow \pi(7)$
					27 200	8 500	l.m.c.t.
				$[Al(bipy^-)_3]$	26 200	8 600	*d*
				$Na^+(bipy^-)$	25 900	17 000	*e*
(IV)	22 500	5 000	m.l.c.t. [$Ru^{III}d(e) \longrightarrow \pi^*(7)$ of bipy] $+\pi(7) \longrightarrow \pi(11)$ of bipy$^-$	$[Ru(bipy)_3]^{3+}$	23 800	1 100	*g*
				$[Ru^{II}(bipy^-)_3]^-$	24 100	4 000	*h*
				$[Ir^{III}(bipy^-)_3]$	21 900	3 000	
				$Na^+(bipy^-)$	23 700	10 000	*e*, Sharp, structured
(V)	18 500	3 000	$\pi(7) \longrightarrow \pi(10)$ of bipy$^-$	$[Ru^{II}(bipy^-)_3]^-$	18 000	5 000	*f*
				$[Ir^{III}(bipy^-)_3]$	19 600	4 000	
				$[Al(bipy^-)_3]$	19 700	2 300	*d*
				$Na^+(bipy^-)$	18 000	4 500	*e*

[a] See Figure. [b] Total observed absorption coefficient. [c] This work or ref. 9 except where indicated. [d] Y. Torii, S. Murasato, and Y. Kaizu, *Nippon Kagaku Zasshi*, 1970, **91**, 541; *Chem. Abstr.*, 1970, **73**, 93426. [e] Ref. 15. [f] Ref. 6. [g] Ref. 14 and this work. [h] Figure of ref. 6.

characteristic of the $Ru^{III}(bipy^-)$ chromophore of (1*), which gives rise to a triplet state (1**), some 42 000 cm^{-1} above the ground state of (1), since (1**) is *ca.* 26 000 cm^{-1} above (1*), by absorption, while (1*) is some 15 000 cm^{-1} above (1), by emission. (1**) is a triplet, since the transition from (1*) to (1**) is spin allowed, and is too high in energy for any $^3(d \longrightarrow d)$ state of (1) (such states are discussed below).

An extra band in this region is also [9] characteristic of the $Ir^{III}(bipy^-)$ system. We must therefore, by elimination, assign the band to an l.m.c.t. process involving higher metal orbitals, such as 5*s*, 5*p* for Ru and 6*s*, 6*p* for Ir, which will be mixed in antibonding combinations with ligand lone pairs, giving the transitions some one-centre character. The proximity of these bands for the $Ru^{III}(bipy^-)$ and $Ir^{III}(bipy^-)$ chromophores is probably fortuitous, and the greater intensity for Ru may indicate a detailed difference of assignment within the general class proposed.

Band (IV) (22 500 cm^{-1}; ε = 5 000 dm^3 mol^{-1} cm^{-1}).—This band was reported by Sutin and Creutz.[2] It is largely the expected $\pi(7) \longrightarrow \pi(11)$ transition of bipy$^-$, with presumably a contribution from a band in the spectrum of $[Ru(bipy)_3]^{3+}$, shown without comment by Mason and co-workers [14] and plausibly assigned as m.l.c.t. [$Ru^{III} \longrightarrow$ bipy $\pi^*(7)$].[9]

Band (V) (18 500 cm^{-1}; ε = 3 000 dm^3 mol^{-1} cm^{-1}).—This band has not hitherto been reported, being fairly weak, at a wavelength where photomultiplier sensitivity is mediocre, and uncomfortably close to the emission of (1*). It cannot be related to the familiar m.l.c.t. ($Ru^{II} \longrightarrow$ bipy) system of (1) since there is no Ru^{II} present in (1*), but is immediately assignable as the $\pi(7) \longrightarrow \pi(10)$ transition of bipy$^-$.

Other Excited States of (1*).—The bipy $\pi(7) \longrightarrow \pi(8,9)$ band of (1*) is confidently predicted, from data for $Li^+(bipy^-)$ [15] and for $Ir^{III}(bipy^-)$ complexes,[9] to lie at around 11 000 cm^{-1}, but to be of low intensity (*ca.* 1 000 or less); for the present, its position, weakness, and overlap with the emission tail of (1) place it below the detection limits of our measurements. The same is true for the lowest bipy $\longrightarrow Ru^{III}$ [$\pi(6) \longrightarrow d(a_1; D_3)$] band, found [14] at 15 000 cm^{-1} (ε = *ca.* 400) in $[Ru(bipy)_3]^{3+}$.

The spin-allowed bipy$^-$ $\longrightarrow d(e\sigma^*)$ charge-transfer bands will generate (1) in its $^3T_1$ or $^3T_2$ ligand-field states (labels in O_h), but with a slightly distorted ligand geometry. Simple energy considerations [9] show that these transitions should lie in the near-i.r., and confirm that the substitution-labile non-emitting decay levels, thermally accessible from (1*) at *ca.* 3 000—4 000 cm^{-1},[16,17] should be assigned to the lower of these states.

An intervalence charge-transfer band (bipy$^-$/bipy) should be shown by (1*). Unfortunately, it would be difficult to observe this directly, since in a range of model compounds [including (1)$^-$] the band lies near 4 000 cm^{-1} and is broad and weak.[18]

Consequences for (1) *and for Emission by* (1*).—It has been known for some time [19] that the emission of (1*), following excitation of (1) by light around 20 000 cm^{-1}, is anomalously highly polarised. Conventionally,[20] an E-absorbing E-emitter shows a maximum polarisation of $\frac{1}{7}$. This is because, within the *x,y* plane, the angle of emission polarisation is random relative to that of the exciting absorption. The *x,y* plane does not on average become anisotropic on absorption, or, if it does, the anisotropy is lost before emission occurs.

Recently, both Hipps,[21] and Carlin and DeArmond,[22] have associated the high photoselection emission polarisation with distortion of (1*) away from D_3 symmetry, and the latter have invoked the excited state pseudo-Jahn–Teller effect; [23] Ferguson and Herren [24] have also invoked localised excitation to explain features of the circular dichroism spectrum. The distortion of (1*) away from D_3 is a natural consequence of promoted electron trapping. The high polarisation values are then demonstrably[9] inevitable, provided that: (*i*) an appreciable proportion of the absorbed light generates an excited state of (1) in a geometrically distorted condition *lower* in energy than the undistorted form, and defining, by its polarisation within the *x,y* plane, which bipy group is the most probable recipient of the promoted electron (This is the physical interpretation of the pseudo-Jahn–Teller effect in this context, and can also be related to Albrecht's[20] concept of a mixed-polarisation transition.); (*ii*) the preference imposed by the initial polarisation is preserved throughout the subsequent processes, including vibrational and spin-orbital relaxation, and formation of the true emitting state; and (*iii*) thermal intervalence hopping in (1*) is not too fast compared with decay to the ground state.

The polarisation anomaly is less marked for $^*[Os(bipy)_3]^{2+}$ than for (1*);[21] we infer that at least one of our three conditions is less effectively met in this case, but cannot from our present data say which.

Conclusions

The absorption of (1*) can be understood in detail, both in position and in intensity, as a superposition of transitions localised in Ru^{III}(bipy) and Ru^{III}($bipy^-$) chromophores, including the appropriate charge-transfer bands. The suggestive resemblance between the spectra of $(1)^-$ and (1*) conceals some informative complexities, which no doubt account for the inconclusiveness of earlier discussions. The formulation of (1*) as $[Ru^{III}(bipy)_2(bipy^-)]^{2+}$, established by excited-state Raman studies, has thus been independently confirmed by a different spectroscopic technique and must be taken as real. The photoselection emission data then imply that the reduced $bipy^-$ retains its separate identity throughout the lifetime of (1*).

Experimental

The spectrum of (1*) was obtained by conventional room-temperature flash photolysis of (1) (as chloride), at a concentration of 2.5×10^{-5} mol dm^{-3} in deoxygenated water in a 1-cm square cross-section cell. Data are averaged over three separate experiments, corrected for emission, and shown to be independent of laser power in the range used. Excitation was by 2.5-mJ 347-nm ruby and 3-mJ 530-nm Nd^{3+} glass lasers, both of pulse length 15 ns, and spectra were measured after 50 ns; effectively no ground-state molecules are present under these conditions.

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