Spectro-electrochemical Studies on Tris-bipyridyl Ruthenium Complexes; Ultra-violet, Visible, and Near-infrared Spectra of the Series $[Ru(bipyridyl)_3]^{2+/1+/0/1-}$

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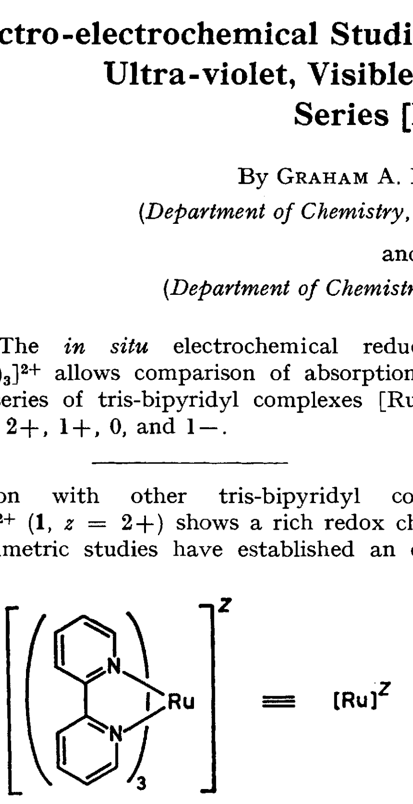
Summary The *in situ* electrochemical reduction of $[Ru(bipy)_3]^{2+}$ allows comparison of absorption spectra for the series of tris-bipyridyl complexes $[Ru(bipy)_3]^z$ with $z = 2+$, $1+$, 0, and $1-$.

In common with other tris-bipyridyl complexes, $[Ru(bipy)_3]^{2+}$ (**1**, $z = 2+$) shows a rich redox chemistry, and voltammetric studies have established an extended sequence of reversible one-electron reduction steps at narrowly spaced potentials, as well as a metal-based oxidation (Table 1).[1,2] The absorption and luminescence spectra of $[Ru(bipy)_3]^{2+}$ have received considerable study, partly owing to this compound's prominence in discussion of suitable redox-active dyes for photogalvanic devices, and in the photocatalysed splitting of water.[3] $[Ru(bipy)_3]^{1+}$ is an intermediate in the reductive quenching of $^*[Ru(bipy)_3]^{2+}$ and there are varying descriptions of the structure and origin of its intense visible absorption.[4-8] $[Ru(bipy)_3]^0$ efficiently reduces H_2O to H_2, in contrast to $[Ru(bipy)_3]^{+}$,[9] and there is an earlier report of electrogeneration of $[Ru(bipy)_3]^0$ and $[Ru(bipy)_3]^{1-}$.[2] However, no spectroscopic data have been published for these lower-oxidation state species.



(**1**)

Table 1. Electrode potentials for $[Ru(bipy)_3]^z$, $E°/V$.[a]

$$[Ru]^{2+} \xrightarrow[-1{\cdot}06]{} [Ru]^{1+} \xrightarrow[-1{\cdot}24]{} [Ru]^{0} \xrightarrow[-1{\cdot}49]{} [Ru]^{1-} \xrightarrow[-2{\cdot}17]{} [Ru]^{2-\,b}$$

[a] *Vs.* standard hydrogen electrode (S.H.E.). [b] $[Ru(bipy)_3]^{2-}$ is short-lived, releasing bipy.[2]

We now report that controlled electrochemical reduction of $[Ru(bipy)_3]^{2+}$ in an optically transparent cell has enabled us to determine the absorption spectra of the individual low-valent complexes over a wide range. A very simple progression in the spectra emerges, and provides fresh insight into the electronic structure of the reduced species.

Solutions of $[Ru(bipy)_3][BF_4]_2$ (1 mmol l^{-1}) in dry acetonitrile, propylene carbonate, or dimethyl sulphoxide containing 0·1 M Bu_4NBF_4 were purged with argon and reduced at a gold minigrid optically transparent thin-layer electrode[10] mounted in a gas-tight poly(tetrafluoroethylene) cell block in the spectrometer beam (Unicam SP800 and Beckman 5270). Steady-state spectra for (**1**) with $z = 1+$, 0, and $1-$, at applied potentials of $-1{\cdot}2$, $-1{\cdot}4$, and $-1{\cdot}7$ V respectively (*vs.* S.H.E.), were recorded in the range 40,000—7,000 cm^{-1} using a Metrohm E506 potentiostat.

A notable finding in the present study is that the fully reduced species $[Ru(bipy)_3]^{1-}$ shows a detailed resemblance in band positions and structure to $[Mo(CO)_4(bipy)]^{1-}$ and Na(bipy), which both contain the chelated $bipy^-$ radical anion.[11,12] It is also apparent from the tabulated data, and particularly from the Figure, that the stepwise reduction is accompanied by *progressive* growth of the bands which typify $[Ru(bipy)_3]^{1-}$, and by matching loss of the bands characterising $[Ru(bipy)_3]^{2+}$, with only minor frequency shifts. In the richer spectra associated with the intermediate complexes, both sets of bands are evidently present. This behaviour is difficult to reconcile with charge-averaged models arising from population of delocalised molecular orbitals spanning three ligands in D_3 symmetry.

On the evidence of the number, position, structure, and intensity of the observed spectral features the reduced ruthenium complexes are most realistically formulated with distinct bipy and $bipy^-$ ligands, *i.e.* as $[Ru(bipy)_2(bipy^-)]^{1+}$, $[Ru(bipy)(bipy^-)_2]^0$, and $[Ru(bipy^-)_3]^{1-}$, respectively. It is then possible to make general assignments of the observed bands in every case, as indicated in Table 2. For example, the prominent band envelope near 20,000 cm^{-1} for $[Ru(bipy)_3]^{1+}$ is dominated by $bipy^-$ internal $\pi \rightarrow \pi^*$ transitions with $M \rightarrow L(bipy^0)$ charge transfer providing only a high energy shoulder,† contrary to previous assignments.[4–8] It also follows that a trapped-electron model $[Ru^{III}(bipy)_2(bipy^-)]^{2+}$ deserves consideration in relation to the spectrum of $^*[Ru(bipy)_3]^{2+}$ which resembles that of Na(bipy) in crucial respects, though a delocalised model has been preferred.[13]

Our observations indicate that $[Ru(bipy)_3]^0$ is a diradical, contrary to the diamagnetic formulation proposed on the basis of early e.s.r. results and a delocalised model.[2] In the case of successive reductions of $[Ir(bipy)_3]^{3+}$, Hanck and his co-workers have drawn similar conclusions from the spacing of the electrode potentials.[14] We note that a similar E^0 sequence exists for $[Ru(bipy)_3]^{2+}$.‡

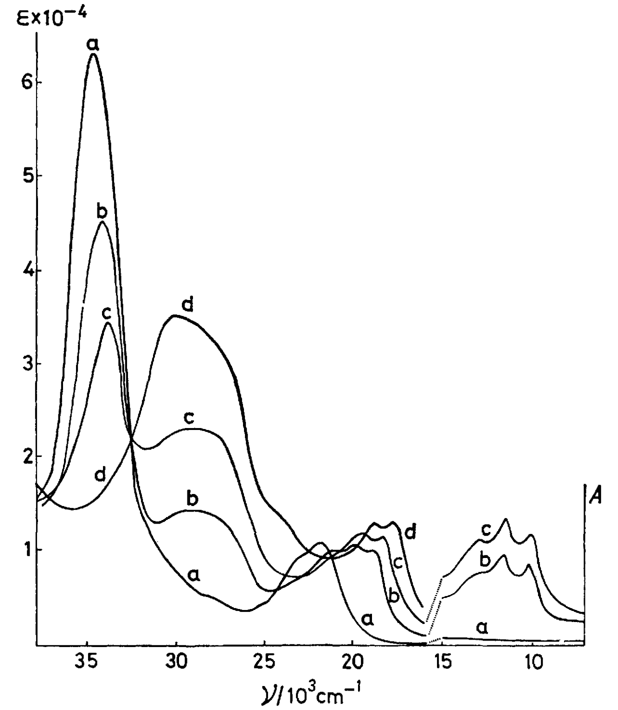


FIGURE. Absorption spectra of $[Ru(bipy)_3]^z$ complexes: (a) $z = 2+$; (b) $z = 1+$; (c) $z = 0$; (d) $z = 1-$; complexes dissolved in dimethyl sulphoxide (u.v.–visible region, ϵ = optical extinction coefficient in $mol^{-1} dm^3 cm^{-1}$) and propylene carbonate (near-i.r. region, A = relative absorbance in arbitrary units).

Interestingly, the lower-valent ruthenium complexes are subject to continuous thermal bleaching (reversion to $[Ru(bipy)_3]^{2+}$) under the experimental conditions of near-i.r. irradiation. Studies are continuing in order to provide extinction coefficients and a definitive near-i.r. spectrum of $[Ru(bipy)_3]^{1-}$, though the trend in spectral features is

TABLE 2. Absorption bands in tris-bipyridyl ruthenium complexes; $\nu/10^3 cm^{-1}$ ($\epsilon \times 10^{-4}$).

	$\pi \rightarrow \pi^*$, bipy	$\pi \rightarrow \pi^*$, $bipy^-$	$M \rightarrow L$, bipy	$\pi \rightarrow \pi^*$, $bipy^-$	$\pi \rightarrow \pi^*$, $bipy^-$
$[Ru(bipy)_3]^{2+}$	35·0(6·12)	—	22·0(1·11)	—	—
$[Ru(bipy)_3]^+$	34·2(4·44)	29·2(1·43)[a]	21·1(1·01)	19·9(1·09) 18·9(1·04)	12·8 11·5 10·1
$[Ru(bipy)_3]^0$	33·8(3·47)	29·0(2·29)[a]	20·8(sh)	19·5(1·20) 18·4(1·18)	12·7 11·1 10·0
$[Ru(bipy)_3]^-$[b]	—	29·8(3·50)[a]	—	18·9(1·26) 18·0(1·28)	not established
Na(bipy)–tetrahydrofuran[12c]	—	25·9(2·95)	—	18·8(0·62) 17·8(0·65)	13·3(0·11) 12·0(0·15) 10·5(0·13)

[a] Probably includes $M \rightarrow L(bipy^-)$ near 30,000 cm^{-1}, consistent with greater breadth *cf.* Na(bipy)[12] and $[Al(bipy)_3]$.[12c] [b] The shoulder near 24,000 cm^{-1} is also present in Na(bipy).[12]

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† The absorption curve for electrogenerated $[Ru]^{1+}$ described elsewhere[5] can be simulated by incomplete reduction or by controlled partial reversion to $[Ru]^{2+}$; isosbestic points coincide exactly with those reported.

‡ *Added in proof:* Independent e.s.r. studies for $[Ru]^z$ ($z < 2$) now support a localised model (K. W. Hanck, A. G. Motten, and K. DeArmond, to be published). We thank Professor Hanck for his personal communication.

clear. Very recently, Elliot has reported near-i.r. (only) spectro-electrochemical data for the more stable series of substituted complexes $[Ru\{4,4'-(CO_2Et)_2bipy\}_3]^z$ (z = 2+, 1+, 0, 1−) which show progressive growth of analogous intense bands near 7,000 cm^{-1}.[15] An unusual interligand charge-transfer was suggested but these bands should now be reassigned as localised $\pi \rightarrow \pi^*$ transitions of the radical bipyridyl anion, as in the parent compounds.

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