# Circular Polarisation of Electrochemiluminescence from Tris-di-imineruthenium(II) Species

**P. M. L. Blok,**[a] **P. S. Cartwright,**[b] **H. P. J. M. Dekkers,***[a] **and R. D. Gillard***[b]

[a] *Gorlaeus Laboratory, Department of Chemistry, Leiden University, P.O. Box 9502, Leiden, The Netherlands*
[b] *Department of Chemistry, University College, P.O. Box 78, Cardiff CF1 1XL, Wales, U.K.*

The circular polarisation of the electrochemiluminescence (ECL) observed from (+)-[Ru(1,10-phenanthroline)$_3$]$^{2+}$ has the same dissymmetry factor (*g*-factor) as does that of emission from the same ion, demonstrating that the ECL arises from the emission of the ruthenium(II) species.

Because they have useful (and fascinating) photochemical properties, salts of complex ions of the type [Ru(LL)$_3$]$^{2+}$ have been studied in great detail.[1] Here, LL = a chelating di-imine, usually N-heterocyclic, like 2,2′-bipyridyl (bipy) or 1,10-phenanthroline (phen). Among the photo-related properties are photoracemization, indications of catalysed photolysis of water, and the remarkable chemiluminescence from the oxidized form containing ruthenium(III) (made chemically or electrochemically) upon reduction. In a recent study,[2] a reaction of the ruthenium(III) species (LL = phen) was said to go through a pseudo-base as intermediate, as postulated previously.

Bard and Rubinstein[3] have been able to generate steady electrochemiluminescence by anodic oxidation of aq. [Ru(bipy)$_3$]$^{2+}$ in the presence of an excess of a chemical reductant (like ethane-1,2-dioate, oxalate) which rapidly restores Ru$^{III}$ to Ru$^{II}$. The electroluminescence for LL = phen was studied recently.[4] In dimethylformamide (DMF) as a solvent with persulphate, the ECL intensity for the complex with LL = bipy was found to be about four times as great as for the phen complex. With our conditions we find rather the opposite.

We have succeeded in generating a strong and steady ECL from a buffered (pH 4.8) aqueous solution of Ru(phen)$_3$$^{2+}$ in an excess of sodium oxalate as follows. Platinum (sheet or gauze) anodes gave luminescence but the observed circular polarisation arose from artefacts due to linear polarisation.[5] Using graphite discs, partially coated with an electrically non-conducting resin, we produced long-lasting ECL without interfering linear polarisation.

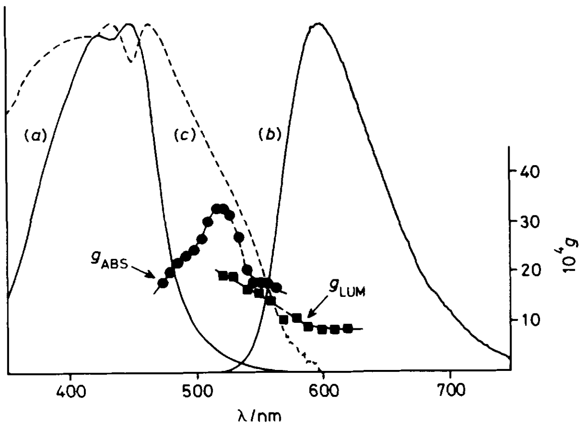

**Figure 1.** (a), Regular absorption spectrum; (b), emission spectrum; (c), logarithm of the excitation spectrum of a very dilute solution of $Ru(phen)_3{}^{2+}(ClO_4)_2$ in buffer; $g_{ABS}$, dissymmetry factor (degree of circular polarisation) in absorption; $g_{LUM}$, dissymmetry factor in luminescence.

This is the first observation of circular polarisation of chemiluminescence generated electrochemically (*i.e.* of ECL) and the first for chemiluminescence from any reaction of a co-ordination compound.

The circular polarisation of the resulting chemiluminescence had several novel features. It does coincide, both in position and in degree (*g* factor), with the circular polarisation (CPL) of 'normal' emission from an aqueous solution of $(+)$-$[Ru(phen)_3]\cdot(ClO_4)_2$, stimulated by light of various wavelengths. This latter CPL spectrum has also been measured for the first time, though the related property for $(+)$-$[Ru(bipy)_3]^{2+}$ is known.[6]

Typically, for $(+)$-$[Ru(phen)_3](ClO_4)_2\cdot 6H_2O$ in water, $g_{ECL}$ (550 nm) $= +12(\pm 2) \times 10^{-4}$ and $g_{ECL}$ (600 nm) $= +6(\pm 1.5) \times 10^{-4}$ (Figure 1). Keeping the band-width the same (40 nm), for the same enantiomer, a normal measurement of the circular polarisation of emission (luminescence) gave $g_{LUM}$ (550) $= +14(\pm 1) \times 10^{-4}$ and $g_{LUM}$ (600) $= +7(\pm 1) \times 10^{-4}$ (Figure 1). Correcting for the partial (and dichroic) re-absorption of the emitted light in ECL, the value of $g_{ECL}$ (550) becomes $+13(\pm 2) \times 10^{-4}$, in excellent agreement with $g_{LUM}$. In the experiment the interference from the circular dichroism[7] of the ruthenium(III) species is unimportant.

The band shapes of ECL and of luminescence are very similar, so it seemed probable that ECL and luminescence are identical.[8] However, the present demonstration that an intensive band property (optical activity) is equal for ECL and luminescence is a conclusive proof of this identity.

A number of points arise in the present work which show that there are several transitions in the long wavelength absorption of tris-1,10-phenanthrolineruthenium(II). The agreement (in the overlap region of absorption and emission) in sign and size of *g* and $g_{LUM}$ suggest that in absorption the transition corresponding to the emission is situated around 550 nm. The overlap of absorption and emission spectra, and the intensity enhancement in the excitation spectrum (also see Figure 1) as compared to the regular absorption spectrum there, support this possibility.

*Received, 16th March 1987; Com. 321*

## References

1 J. Ferguson and E. Krausz, *Inorg. Chem.*, 1986, **25**, 3335; S. F. McClanahan and J. R. Kincaid, *J. Am. Chem. Soc.*, 1986, **108**, 384 and references cited therein.
2 D. Kotkar, V. Joshi, and P. K. Ghosh, *Inorg. Chem.*, 1986, **25**, 4334.
3 I. Rubinstein and A. J. Bard, *J. Am. Chem. Soc.*, 1981, **103**, 512.
4 F. Bolletta, M. Ciano, V. Balzani, and N. Serpone, *Inorg. Chim. Acta*, 1982, **62**, 207.
5 H. P. J. M. Dekkers, P. F. Moraal, J. M. Timper, and J. P. Riehl, *Appl. Spectrosc.*, 1985, **39**, 818, describes artefacts in CPL measurements arising, *inter alia*, from linear polarisation.
6 H. P. J. M. Dekkers and R. D. Gillard, unpublished work, 1981; A. Gafni and I. Z. Steinberg, *Isr. J. Chem.*, 1976, **15**, 102.
7 J. A. A. Sagues, R. D. Gillard, R. J. Lancashire, and P. A. Williams, *J. Chem. Soc., Dalton Trans.*, 1979, 193.
8 N. E. Tokel-Takvoryan, R. E. Hemingway, and A. J. Bard, *J. Am. Chem. Soc.*, 1973, **95**, 6582.