Electrochemistry and Near Infrared Spectroscopy of Tris(4,4'-dicarboxyethyl-2,2'-bipyridine)ruthenium(II)

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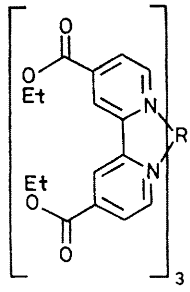
Summary Near i.r. transitions similar to those observed for type II mixed valence compounds are observed for the electrochemically reduced monomeric complex tris(4,4'-dicarboxyethyl-2,2'-bipyridine)ruthenium(II) bishexafluorophosphate



(1)

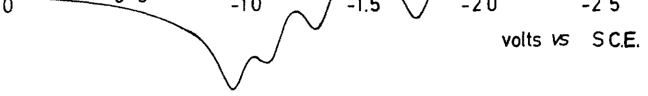


Figure 1. Cyclic voltammagram of (**1**) at a platinum electrode in 0·1 M $TBAPF_6$/acetonitrile.

The electrochemical reduction and subsequent spectral examination of tris(4,4'-dicarboxyethyl-2,2'-bipyridine)-ruthenium(II) ion (**1**) have resulted in the observation of some interesting and unusual results. First, apparently because of the the electron withdrawing nature of the CO_2Et groups and the enhanced ability for electron delocalization in the ligand, the potentials for each of several sequential one electron reductions in (**1**) are shifted anodically, relative to the unsubstituted bipyridine complex. The shift is sufficient to allow six quasi-reversible-to-reversible one-electron (by coulometry) reductions to be observed in acetonitrile. A cyclic voltammogram of (**1**) is shown in Figure 1. $E_{\frac{1}{2}}$ Values from the cyclic voltammetry of (**1**) are compared to $E_{\frac{1}{2}}$ values for the analogous 5,5'-dicarboxyethyl substituted complex,[1a] and the unsubstituted bipyridine complex in the Table.[1b] The simple observation of this extent of reversible electrochemistry from a complex containing a single metal is itself unusual.

Table. Tris(4,4'di-R^1-5,5'-di-R^2-2,2'-bipyridine) ruthenium(II)

Redox couple	$R^1 = CO_2Et$, $R^2 = H$	$R^1 = H$,[a] $R^2 = CO_2Et$	$R^1 = H$,[b] $R^2 = H$
+2/+1	−0·98	−0·82	−1·25
+1/0	−1·10	−0·93	−1·43
0/−1	−1·42	−1·23	−1·68
−1/−2	−1·76	−1·76	−2·30
−2/−3	−1·95	−1·92	—
−3/−4	−2·22	−2·24	—

[a] See ref. 1a. [b] Polarographic $E_{1/2}$ *vs.* s.c e. values obtained in dimethylformamide. See ref. 1b.

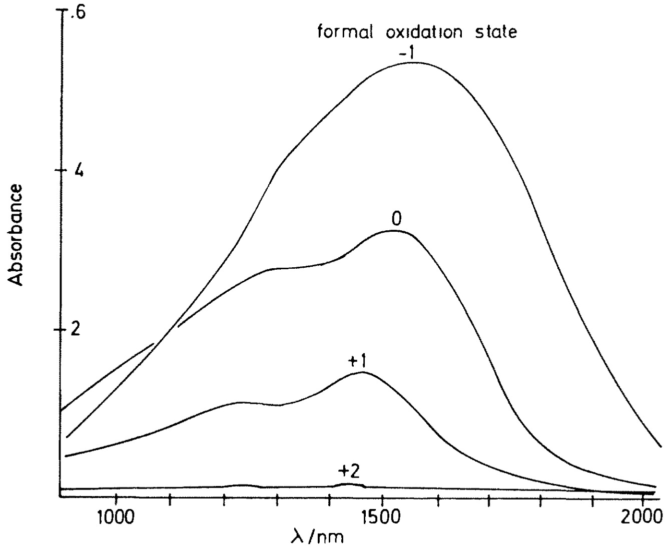


FIGURE 2. Near i.r. spectra of (**1**) in 0·4 mM solution in acetonitrile, 0·1 M $TBAPF_6$, measured in a 1 mm cell.

In addition to the simple electrochemistry, preliminary studies were conducted on the reduction products of (**1**), by means of the optically transparent thin layer electrode technique (OTTLE)[2] and by controlled potential coulometry. Spectra obtained for all six reduction products from the OTTLE experiment† and for the first five reduction products in the bulk coulometry experiment produced a result previously unreported for monomeric metal complexes. In the region between 700 and 2100 nm, the spectrum of (**1**) shows no absorption, as would be expected. However, upon reduction by one electron a very broad pair of overlapping peaks appear with maxima at 1210 ($\epsilon = 2600$) and 1460 nm ($\epsilon = 3400$). With the second one-electron reduction, the peaks shift to slightly lower energy (1290 and 1510 nm) and increase in intensity ($\epsilon = 6000$ and 7300). With the third electron reduction, the two peaks coalesce into a broad absorption at 1560 nm which is again enhanced in intensity ($\epsilon = 12000$). Upon reduction by the fourth and subsequent electrons the peak intensity diminishes continuously to approximately zero for the six electron product.†

Historically such near i.r. bands have been associated with intervalence electron transfers between metal centres in mixed valence, bis-metal systems such as the well known Ru^{2+}/Ru^{3+} Creutz and Taube ion.[3] We have tentatively assigned the transitions in the reduced forms of (**1**) to either inter- or intra-ligand charge transfer transitions or a combination. To our knowledge this is the first example of a metal complex which exhibits such a transition without directly involving an electron transfer between two metal centres in different oxidation states.

The observation of near i.r. transitions for the various formal oxidation states of (**1**) raises questions about how widespread the phenomena might ultimately prove to be among metal complexes. The question is also raised about whether similar behaviour might be exhibited by the reduced form of the free ligand or possibly by the analogous *NN'*-dialkyl-bipyridine.

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† Owing to the rather large changes in solution density associated with the significant charge change occurring upon reducing the complex (by 4, 5, and 6 electrons), a significant amount of convective stirring was observed in the cell. Because of this phenomenon, the spectra obtained for these three oxidation states were considered to be only of qualitative value.

[1] (a) C. M. Elliott and J. A. Harding, unpublished results; (b) T. Saji and Aoyagui, *J. Electroanalyt. Chem.*, 1975, **58**, 401.

[2] R. W. Murray, W. R. Heineman, and G. W. O'Dom, *Anal. Chem.*, 1967, **39**, 1666.

[3] C. Creutz and H. Taube, *J. Amer. Chem. Soc.*, 1969, **91**, 3988.