Inorganica Chimica Acta, *82* (1984) 149–151

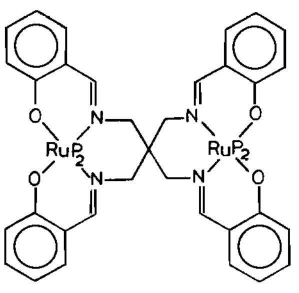
Mono- and Binuclear Ruthenium(II) Schiff-Base Complexes: Spectrophotometric and Electrochemical Studies

HIDEO DOINE, FRANK F. STEPHENS and RODERICK D. CANNON*

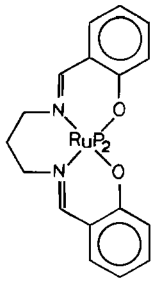
School of Chemical Sciences, University of East Anglia, Norwich NR4 7TJ, U.K.

Received June 14, 1983

As part of a study of electron transfer processes in mixed-valence binuclear complexes, we report here results of electrochemical and spectrophotometric studies of the complex I, and of its mononuclear analogue II ($P = P(C_6H_5)_3$).



I



II

In the semi-oxidised $Ru^{III}\cdots Ru^{II}$ *complex corresponding to* I, *we find evidence of a small extent of interaction between the Ru atoms, as reflected in the comproportionation constant* K_{com} *(eqn. 1).*

$$Ru^{III}\cdots Ru^{III} + Ru^{II}\cdots Ru^{II} \overset{K_{com}}{\rightleftharpoons} 2Ru^{III}\cdots Ru^{II} \qquad (1)$$

but the corresponding intervalence charge transfer spectrum is not detected.

Experimental

Materials

Complex I

The ligand was prepared from tetraaminomethylmethane (TAM) [1] by the method of Oehmke and Bailar [2] and recrystallised from benzene. The complex $Ru(PPh_3)_3Cl_2$ [3] (0.10 g) was added under nitrogen to a solution of the ligand (0.055 g) and 1 ml Et_3N in 50 ml toluene and refluxed for four days. Samples taken every 2–5 hours showed the gradual disappearance of IR bands at 1625 and 1585 cm^{-1} and appearance of bands at 1600 cm^{-1} and 1525 cm^{-1}. On removing the solvent a brown-green solid remained which was repeatedly recrystallised under nitrogen, from toluene–petroleum mixtures.

Complex II

The ligand was prepared by reacting salicylaldehyde and 1:3 propanediol in 2:1 ratio on a steam bath for 30 mins. To partially remove water, ethanol was added, then removed on the rotary evaporator. Cooling in ice gave dark yellow crystals, recrystallised from ethanol. Found: C 72.3, H 6.46, N 9.91%; Calc: for $C_{17}H_{18}N_2O_2$, C 72, 3, H 6.38, N 9.93%.

The complex $Ru(PPh_3)_2Cl_2$ (0.20 g) was added under nitrogen to a solution of the ligand (0.06 g) and Et_3N (1.0 ml), in 100 ml THF, in a flask with a sintered glass filter outlet already attached. After refluxing 2 hr, the solution was filtered to remove Et_3NHCl, the solvent was removed, the product was pumped dry and recrystallised from THF and petroleum (40–60).

Found: C 69.5 H 5.75, N 4.27; Calc. for $C_{105}H_{88}N_4O_4P_4Ru_2$: C 70.2, H 4.90, N 3.12%. Even in the solid state, the complex is extremely air-sensitive.

Measurements

Cyclic voltammograms were obtained with the PAR 175 Universal Programmer and 174A Polarographic Analyser, using bright platinum working electrodes and a reference electrode of Ag wire/$AgNO_2$ in CH_3CN, connected to the cell compartment by a salt bridge of the working solvent saturated with n-Bu_4NClO_4. All measurements were carried out in the medium of 0.1 *M* n-Bu_4NClO_4, at 26 °C, under an atmosphere of nitrogen scrubbed in succession with aqueous chromium(II) and the appropriate

---

*Author to whom correspondence should be addressed.

0020-1693/84/$3.00

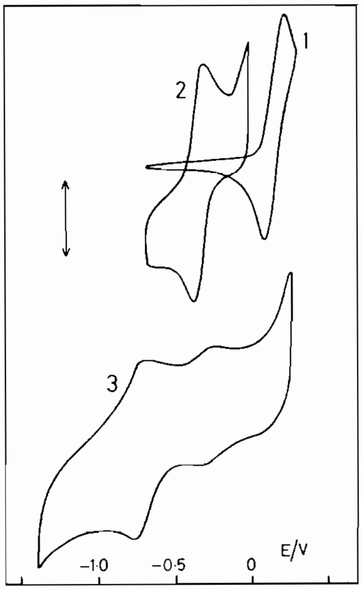


Fig. 1. Cyclic voltammograms (1) Ferrocene, 5 × 10^{-4} *M*, vertical double arrow denoting 200 μA; (2) complex *II*, 1.0 × 10^{-4} *M*, 10 μA; (3) complex *I*, 7.5 × 10^{-4} *M*, 10 μA solvent 30% THF, 70% methanol; 0.1 *M* (N-Bu_4N)(ClO_4). Values of E are relative to Ag/Ag^+. Sweep rate 200 mV s^{-1}.

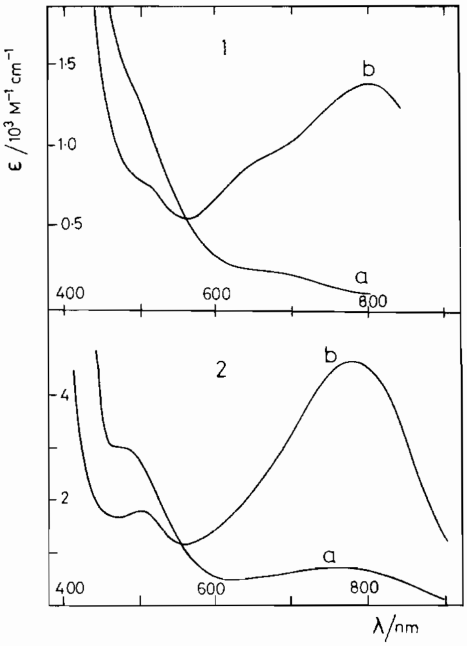


Fig. 2. Absorption spectra of (1, a) complex *I* (1, b) oxidised form; (2,a) complex *II* (2,b) oxidised form. Methanol, 25 °C.

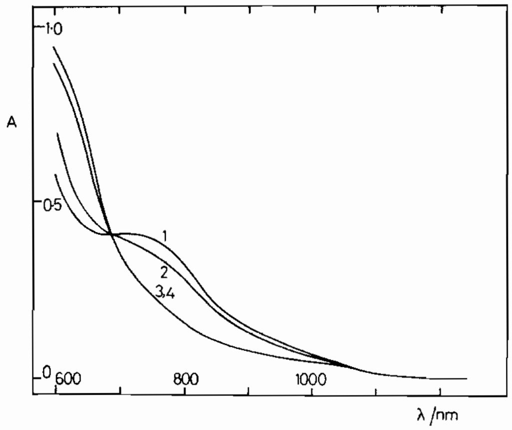


Fig. 3. Spectrophotometric titration of II (initially air-oxidised, curve 1) with Co(sepulchrate)$^{2+}$. Curve 2, $[Co]_T/[Ru_2]_T$ = 0.3; Curves 3, 4 (indistinguishable above 700 nm), $[Co]_T/[Ru_2]_T$ = 0.6, 1.2.

solvent. Potentials reported here are relative to n.h.e. standardised with reference to ferrocene in the same medium (*cf.* Fig. 1) and taking $E^\circ(Fc^+/Fc)$ = 0.400 V in all media [4].

Results and Discussion

Cyclic voltammetry of II showed a single wave, reversible in methanol ($E_{1/2}$ = –0.085 V, peak-to-peak separation E_{pp} = 60V) and quasi-reversible in methanol–THF mixtures. ($E_{1/2}$ = +0.10 V, ΔE_{pp} = 80 mV in 30% THF). As with the analogous ethylenediamine-based complex [5], this signal is assigned to the $Ru^{III/II}$ couple. For the binuclear complex I two overlapping signals were observed, as shown in Fig. 1. The two pairs of peaks are clearly distinguished and no others appear in the range studied. Wave height is proportional to Ru concentration. From the peak potentials we obtain $E_{1/2(1)}$ = –0.020 V, $\Delta E_{pp(1)}$ = 86 mV; $E_{1/2(2)}$ = –0.46 V, $\Delta E_{pp(2)}$ = 80 mV.

Visible absorption spectra of I and II, and of their fully air-oxidised products, are shown in Fig. 2. The spectra of the mononuclear complex II closely resemble those of the ethylenediamine analogue [5], and those of the binuclear complex have bands at similar wavelengths. A careful study was made of solutions of the partially oxidised form of II, in order to detect an intervalence charge transfer of the mixed valence species $Ru^{III}\cdots Ru^{II}$, but none was found. Spectra were obtained by titrating cobalt-(II) sepulchrate [6] into the oxidised $Ru^{III}\cdots Ru^{III}$ form of II. The reduction potentials are such as to ensure that when 1 mol of Co^{II} is added per mol of ruthenium dimer, the mixed valence complex is the predominant species. The sensitivity of both reagents to side-oxidation made it difficult to achieve precise stoichiometry, but a sharp isosbestic point was observed (Fig. 3) and it is clear that from λ = 700–1200 nm there is no significant absorption specific to the mixed-valence species. Maximum limits of extinction coefficient of an IT band are *ca.* 20 M^{-1} cm^{-1}.

Acknowledgements

This work was supported by the Science and Engineering Research Council and the Royal Society. HD held a Monbusho (Japan) Visiting Studentship.

References

1 A. Litherland and F. G. Mann, *J. Chem. Soc.*, 1588 (1938). This preparation was found to give very low yields unless reaction temperature and other conditions were very closely controlled. Further details may be had from the present authors, at the address shown above.
2 R. W. Oehmke and J. C. Bailar, *J. Inorg. Nucl. Chem., 27,* 2199 (1965).
3 T. A. Stephenson and G. Wilkinson, *J. Inorg. Nucl. Chem., 28,* 945 (1966).
4 R. R. Gagné, C. A. Koval, T. J. Smith and M. C. Cimolino, *J. Am. Chem. Soc., 101,* 4571 (1979).
5 H. Doine, F. F. Stephens and R. D. Cannon, to be published.
6 I. I. Creaser, J. M. Harrowfield, A. J. Herlt, A. M. Sargeson and J. Springborg, *J. Am. Chem. Soc., 99,* 3182 (1977); J. MacB. Harrowfield, A. J. Herlt, A. M. Sargeson and T. Del Donno, *Inorg. Synth., 20,* 85 (1982).