Influence of Co-ordination Number on Copper(I)–Copper(II) Redox Interconversions. Part 3.† Reduction of a Sterically Constrained Bis-(substituted phenanthroline) Complex of Copper(II) by Iron(II) and Ruthenium(II) Complexes

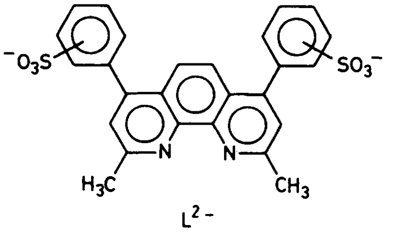
By **Peter Leupin, Najat Al-Shatti, and A. Geoffrey Sykes,*** Department of Inorganic Chemistry, The University, Newcastle upon Tyne NE1 7RU

Further kinetic studies are reported for reduction of the copper(II) complex, $[CuL_2]^{2-}$, containing the ligand L^{2-} = 2,9-dimethyl-4,7-bis[(sulphonyloxy)phenyl]-1,10-phenanthroline. The methyl substituents in the 2,9 positions create a steric hindrance which limits the extent of co-ordination to Cu^{II} (bis and not tris complexes are formed) and five- and four-(tetrahedral) co-ordinate complexes are believed to be present. With $[Fe(CN)_6]^{4-}$, $[Fe(edta)]^{2-}$ (edta = ethylenediaminetetra-acetate), $[Fe(CN)_5(PPh_3)]^{3-}$, and $[Ru(NH_3)_5(pyz)]^{2+}$ (pyz = pyrazine) as reductants (abbreviation Red) limiting kinetics are observed, and a self-consistent interpretation is possible in terms of the sequence: $Cu^{II} \rightleftharpoons {}^{*}Cu^{II}$ (k_1,k_{-1}); Red + $^{*}Cu^{II} \longrightarrow$ products (k_2), and Red + $Cu^{II} \longrightarrow$ products (k_3). In this sequence Cu^{II} and $^{*}Cu^{II}$ are the five- and four-co-ordinate forms respectively. The step k_3 is additional to the sequence previously proposed for $[Fe(CN)_6]^{4-}$, the results for which have been modified accordingly. Contributions from k_3 are not apparent with $[Fe(CN)_5(PPh_3)]^{3-}$ and $[Ru(NH_3)_5(pyz)]^{2+}$, whereas with $[Ru(NH_3)_5(py)]^{2+}$ (py = pyridine) reaction *via* k_3 appears to be dominant. Possible explanations of the balance between k_2 and k_3 in terms of different $E^{\ominus}$ values and ability to react inner-sphere are considered

IT has been demonstrated that 2,9-dimethyl substituents on 1,10-phenanthroline provide a steric hindrance which in the case of Cu^{II} excludes square-planar and octahedral geometries.[1,2] The limiting kinetics previously observed in the $[Fe(CN)_6]^{4-}$ reduction of $[CuL_2]^{2-}$, where L^{2-} is a substituted phenanthroline ligand (see below), are consistent with participation of five- and four-co-ordinate forms of Cu^{II}.[3] Here we report further studies with the iron(II) complexes $[Fe(edta)]^{2-}$ and $[Fe(CN)_5(PPh_3)]^{3-}$ and ruthenium(II) complexes $[Ru(NH_3)_5(pyz)]^{2+}$ and $[Ru(NH_3)_5(py)]^{2+}$ as reductants,‡ and consider elaborations on the mechanism previously proposed. For a previous study using $[Fe(edta)]^{2-}$ as reductant see, for example, ref. 4.

EXPERIMENTAL

Preparation of the Copper(II) *Complex*.—The $[CuL_2]^{2-}$ complex was generated in solution by mixing weighed amounts of $Cu(ClO_4)_2{\cdot}6H_2O$ (G. F. Smith) and the acid form of the ligand L^{2-} = 2,9-dimethyl-4,7-bis[(sulphonyloxy)-phenyl]-1,10-phenanthroline (Sigma), which was generally in eight-fold excess of the stoicheiometric amount required by the formula $[CuL_2]^{2-}$. All other relevant details were as described previously.[3]



L^{2-}

$[Fe(edta)]^{2-}$.—A 1.0×10^{-2} M § stock solution of the iron(II)–edta complex[4] was prepared by dissolving disodium dihydrogen ethylenediaminetetra-acetate dihydrate (B.D.H., AnalaR) (0.39 g) in water, and the solution deoxygenated by bubbling N_2 through for *ca.* 1 h. Air-free ammonium iron(II) sulphate $(NH_4)_2SO_4{\cdot}FeSO_4{\cdot}6H_2O$ (B.D.H., AnalaR) (0.39 g) solution was added, and the volume adjusted to 100 ml. Solutions of $[Fe(edta)]^{2-}$ (colourless) are extremely sensitive to O_2 (yellow colouration), and rigorous air-free techniques (Atlas nylon syringes, stainless-steel needles, rubber seals) were required in all transferences.

$[Fe(CN)_5(PPh_3)]^{3-}$.—A crystalline sample was prepared from the sodium salt of amminepentacyanoferrate(II)[5] by a method described[6] (Found: C, 48.7; H, 3.6; N, 12.7; P, 5.5. Calc. for $Na_3[Fe(CN)_5\{P(C_6H_5)_3\}]{\cdot}2H_2O$: C, 49.9; H, 3.5; N, 12.6; P, 5.7%).

$[Ru(NH_3)_5(pyz)]^{2+,3+}$.—The penta-amminepyrazineruthenium(II) perchlorate complex, $[Ru(NH_3)_5(pyz)](ClO_4)_2$, was prepared by the method of Creutz and Taube.[7] Details of the spectrum, $\lambda_{max.}$ 254 nm (ε 6.5×10^3 M^{-1} cm^{-1}), and 473 nm (ε 11.9×10^3 M^{-1} cm^{-1}), were as previously reported. The ruthenium(III) complex, $[Ru(NH_3)_5(pyz)](pts)_3$ (pts = *p*-toluenesulphonate), also isolated as a solid, was prepared by oxidation of Ru^{II} with lead(IV) dioxide.[7]

$[Ru(NH_3)_5(py)]^{2+}$.—Penta-amminechlororuthenium(III) dichloride, $[Ru(NH_3)_5Cl]Cl_2$, was first prepared.[8] To an amount of this complex (0.10 g) a solution of Ag^I (2 ml), prepared by dissolving silver(I) oxide (0.075 g) in hot water (2 ml) with the addition of trifluoroacetic acid (0.25 ml),[9] was added. Silver chloride was removed by filtration, and reduction to Ru^{II} achieved by reacting with amalgamated zinc shot under N_2 and in the presence of a 25-fold excess of pyridine (0.9 g).¶ After 30 min the Zn/Hg was filtered off and saturated $NaClO_4$ (2 ml) added to precipitate the complex $[Ru(NH_3)_5(py)]^{2+}$. The crude salt was recrystallized from a methanol (35 ml) and water (5 ml) solution, to give $[Ru(NH_3)_5(py)](ClO_4)_2$, with u.v.–visible spectrum, $\lambda_{max.}$ 245 nm (ε 5.14×10^3 M^{-1} cm^{-1}) and 407 nm (ε 7.76×10^3 M^{-1} cm^{-1}) (Found: C, 12.9; H, 4.1; N, 17.8. Calc.: C,

---

† Part 2 is ref. 3.

‡ edta = Ethylenediaminetetra-acetate(4−), pyz = pyrazine, and py = pyridine.

§ Throughout this paper: M = mol dm^{-3}; ml = cm^3.

¶ Complexes with nicotinamide and methyl nicotinate in place of pyridine can be prepared using the same procedure.[9]

12.9; H, 4.3; N, 18.1%). The 407 nm but not the 245 nm (ε 4.62 × 10^3 M^{-1} cm^{-1}) peak is in excellent agreement with the literature (previous ε 7.78 × 10^3 M^{-1} cm^{-1} at 407 nm).[9] Repeated recrystallizations gave self-consistent values.

Reaction of edta with the Copper(II) *Complex*.—The reaction of uncomplexed edta with the $[CuL_2]^{2-}$ complex was investigated briefly because of the possible relevance to the study with $[Fe(edta)]^{2-}$ which is the only substitution labile reductant. The concentration of the copper(II) complex was 1.0 × 10^{-4} M, with L^{2-} in excess at 3.0 × 10^{-4} M, pH 8.0 (10^{-2} M borate), and I = 0.10 M ($LiClO_4$). At 25 °C with 10^3[edta] = 0.20, 0.50, 1.00, 2.50, and 4.50 M, rate constants for the increase in absorbance at 735 nm were 11, 26, 36, 53, and 58 s^{-1} respectively. A limiting rate constant of 58 s^{-1} is observed at [edta] > 4 × 10^{-3} M. On increasing the concentration of the L^{2-} ligand three-fold the observed rate constant at [edta] = 5 × 10^{-4} M was halved. These observations are consistent with a mechanism $[CuL_2]^{2-} \rightleftharpoons CuL + L^{2-}$, $CuL + edta \longrightarrow$ product. It is concluded that at much smaller edta concentrations contributions from reaction paths involving reactions of free edta with the copper(II) complex are $\leqslant$11 s^{-1} and can be neglected.

Kinetic Studies.—All runs were carried out at pH 8.0, using either sodium tetraborate (Fisons, A.R.) (10^{-2} M) or collidine (2,4,6-trimethylpyridine) (B.D.H., Lab. Reag.) (0.020 M) buffers. Satisfactory agreement was obtained in both buffers. The ionic strength was adjusted to I = 0.10 M ($LiClO_4$). All observations are consistent with a single electron transfer and 1 : 1 stoicheiometries, *e.g.* as in (1).

$$Cu^{II} + Fe^{II} \longrightarrow Cu^{I} + Fe^{III} \qquad (1)$$

Formation of $[Cu^IL_2]^{3-}$ was monitored at the 483 nm (ε 12.3 × 10^3 M^{-1} cm^{-1}) peak for all but the $[Ru(NH_3)_5(pyz)]^{2+}$ reduction, which was followed at 400 nm (peak position for Ru^{II}, ε 6.6 × 10^3 M^{-1} cm^{-1}). The reductant was generally in >10-fold excess of the Cu^{II}. A Dionex-D110 stopped-flow spectrophotometer was used with a logarithmic amplifier the output of which was either photographed from an oscilloscope or stored digitally with a Datalab DL901 transient recorder.[10] A Commodore PET 2001-16K was interfaced to the recorder and a simple program used to display absorbance change $\ln(A_\infty - A_t)$ against time. Such plots were linear to at least three half-lives (except in those cases in which the reactant ratio was less than 10 : 1), and the slopes corresponded to first-order rate constants $k_{obs.}$. The $[Ru(NH_3)_5(py)]^{2+}$ reaction was too fast to monitor under other than second-order conditions with equal concentrations of reactions. Plots of $1/(A_\infty - A_t)$ against time for the last 40% of reaction were linear and gave estimates of rate constants.

RESULTS

TABLE 1

The dependence of first-order rate constants (25 °C), $k_{obs.}$, for the reduction of the complex $[CuL_2]^{2-}$ (1 × 10^{-5} M) on reductant concentration at pH 8.0, I = 0.10 M ($LiClO_4$)

10^5 $[Fe(edta)^{2-}]$/M	5.0	7.5	10.0	15.0	20.0	
$k_{obs.}/s^{-1}$ [a]	67	82	111	145	178	
10^5 $[Fe(CN)_5(PPh_3)^{3-}]$/M	5.0	8.0	10.0	15.0		
$k_{obs.}/s^{-1}$ [b]	56	71	81	88		
10^5 $[Ru(NH_3)_5(pyz)^{2+}]$/M	5.0	6.0	7.5	10.0	12.0	18.0
$k_{obs.}/s^{-1}$ [c]	27	33	39	46	52	63
	20.0	25.0	30.0			
	66	66	68			

[a] Borate buffer, λ 483 nm. [b] Collidine buffer, λ 483 nm. [c] Borate buffer, λ 400 nm.

Certain aspects of the rate law have already been established for the $[Fe(CN)_6]^{4-}$ reduction of $[CuL_2]^{2-}$.[3] First-order rate constants, $k_{obs.}$, for the reaction of $[CuL_2]^{2-}$ with three other reductants, $[Fe(edta)]^{2-}$, $[Fe(CN)_5(PPh_3)]^{3-}$, and $[Ru(NH_3)_5(pyz)]^{2+}$ (reductant in large excess), are listed in Table 1. As in the previous study the kinetics are not first-order in reductant, Figure 1. Plots of $(k_{obs.})^{-1}$ against the reciprocal reductant concentration $[Red]^{-1}$ are linear, Figure 2. These observations are consistent with the dependence (2),

$$k_{obs.} = \frac{k_1k_2[Red]}{k_{-1} + k_2[Red]} \qquad (2)$$

which is derived from the mechanism (3)—(4). From (2)

$$Cu^{II} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} {}^*Cu^{II} \qquad (3)$$

$$Red + {}^*Cu^{II} \xrightarrow{k_2} products \qquad (4)$$

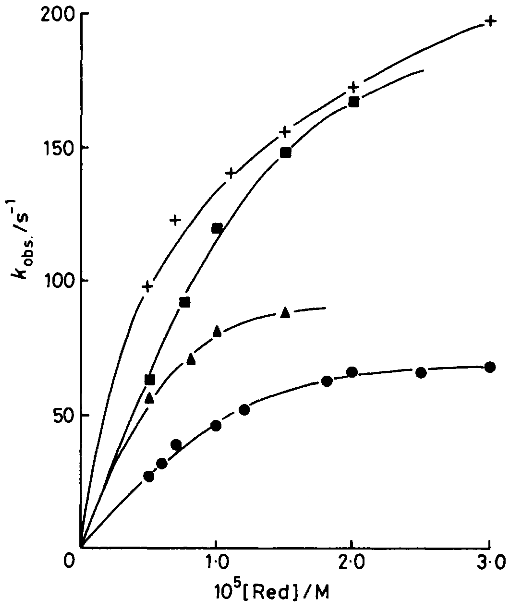


FIGURE 1 The variation of first-order rate constants, $k_{obs.}$, with concentration of reductant $[Fe(CN)_6]^{4-}$ (ref. 3) (+), $[Fe(edta)]^{2-}$ (■), $[Fe(CN)_5(PPh_3)]^{3-}$ (▲), and $[Ru(NH_3)_5(pyz)]^{2+}$ (●) for the reduction of $[CuL_2]^{2-}$ at pH 8.0, I = 0.10 M ($LiClO_4$), and 25 °C

k_1 and k_2/k_{-1} can be evaluated, Table 2. Different k_1 values are obtained however, a fact which is also apparent by inspection of Figure 1 when different limiting plateau rate constants are observed. Therefore a further step (5) is included in the scheme, and the rate expression modified

$$Red + Cu^{II} \xrightarrow{k_3} products \qquad (5)$$

accordingly, (6). Values of k_3 were inserted to give identical

$$k_{obs.} = \frac{k_1k_2[Red]}{k_{-1} + k_2[Red]} + k_3[Red] \qquad (6)$$

intercepts (*i.e.* $1/k_1$ values), Figure 3. From the range of k_3 values giving acceptable linear fits for each reductant those

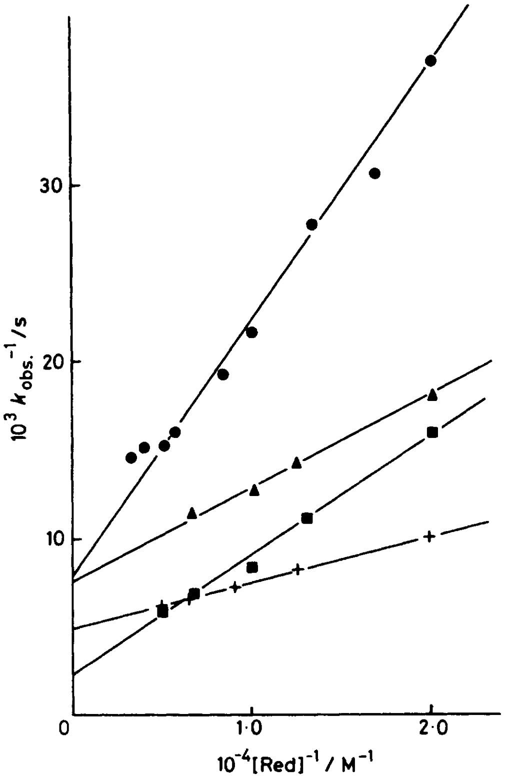


FIGURE 2 The dependence of the reciprocal of the first-order rate constant, $k_{obs.}$, on the reciprocal of the concentration of reductant for the reduction of $[CuL_2]^{2-}$ with $[Fe(CN)_6]^{4-}$ (ref. 3) (+), $[Fe(edta)]^{2-}$ (■), $[Fe(CN)_5(PPh_3)]^{3-}$ (▲), and $[Ru(NH_3)_5(pyz)]^{2+}$ (●) at pH 8.0, $I = 0.10$ M ($LiClO_4$), and 25 °C

giving identical intercepts to other reductants are quoted in Table 3. In other words the prime aim has been to provide a self-consistent interpretation. Modified k_1 and k_2/k_{-1} rate constants with least-squares fits are also listed in Table 3. Some variation (*ca.* ±10%) in k_3 is possible and to this extent rate constants in Table 3 should not be regarded as fixed.

TABLE 2

Summary of data obtained for the reduction of the $[CuL_2]^{2-}$ complex at 25 °C, pH 8.0, and $I = 0.10$ M ($LiClO_4$); treatment excluding k_3 step

Reductant	$E^\ominus$ / V	k_1 / s^{-1}	$10^{-3}k_2/k_{-1}$ / M^{-1}
$[Fe(CN)_6]^{4-}$	0.41 [a]	229	14.6
$[Fe(edta)]^{2-}$	0.12 [b]	440	3.2
$[Fe(CN)_5(PPh_3)]^{3-}$	0.54 [c]	130	1.5
$[Ru(NH_3)_5(pyz)]^{2+}$	0.49 [d]	136	5.1
$[Ru(NH_3)_5(py)]^{2+}$	0.26 [e]	[f]	—

[a] Ref. 3. [b] R. Belcher, D. Gibbons, and T. S. West, *Anal. Chim. Acta*, 1955, **12**, 107. [c] Ref. 12. [d] Ref. 7. [e] Average of two values reported by D. Cummins and H. B. Gray, *J. Am. Chem. Soc.*, 1977, **99**, 5158. [f] See Table 3 for second-order rate constant.

A further reactant $[Ru(NH_3)_5(py)]^{2+}$ was investigated. With one exception this reductant is stronger than others considered, see $E^\ominus$ values in Table 2, and appears to react many times faster than can be accounted for by a sequence in which k_1 has a controlling influence. Only by working with both reactants at a low level (*ca.* 1 × 10^{-5} M) was it possible to pick up the last *ca.* 40% of reaction. The kinetics with concentrations of reactants equal, range (0.5—1.8) × 10^{-5} M, conform reasonably well to a second-order rate law, in which case k_3 is presumed to be the only contributory reaction path, $k_3 = (1.4 \pm 0.3) \times 10^7$ M^{-1} s^{-1}.

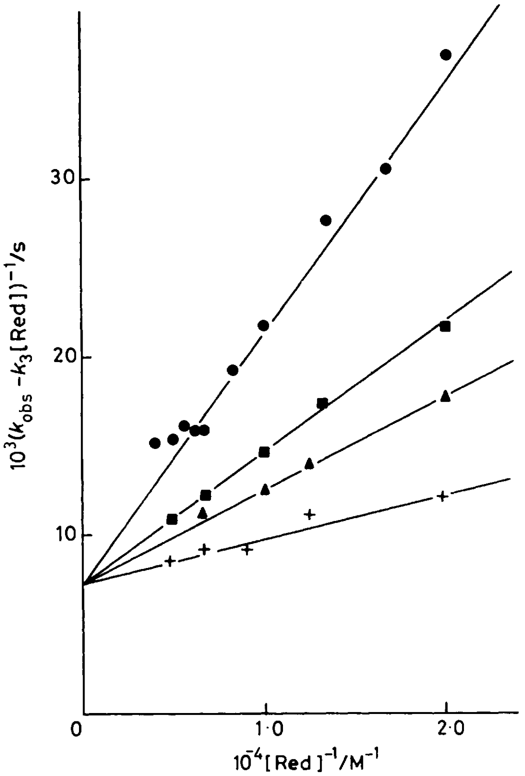


FIGURE 3 Modified reciprocal plots (as in Figure 2) with the inclusion of the k_3 term, at pH 8.0, $I = 0.10$ M ($LiClO_4$), and 25 °C

However, the precision of absorbance data for the final stages of a reaction does not enable us to exclude first-order kinetics, in which case a first-order rate constant (10—50 s^{-1}) is obtained. It is not clear to what process such a value would correspond, since it clearly cannot be k_{-1} with k_1 at 137 s^{-1} and the stationary-state approximation applying in the derivation of (2).

TABLE 3

Summary of data obtained for the reduction of the $[CuL_2]^{2-}$ complex at 25 °C, pH 8.0, and $I = 0.10$ M ($LiClO_4$); treatment including k_3 step

Reductant	k_1 / s^{-1}	10^{-3} k_2/k_{-1} / M^{-1}	k_3 / M^{-1} s^{-1}
$[Fe(CN)_6]^{4-}$	137 ± 7	31.8 ± 4.0	2.7 × 10^5
$[Fe(edta)]^{2-}$	139 ± 11	9.7 ± 1.4	4.2 × 10^5
$[Fe(CN)_5(PPh_3)]^{3-}$	130 ± 10	15.3 ± 1.8	*
$[Ru(NH_3)_5(pyz)]^{2+}$	136 ± 24	5.1 ± 1	*
$[Ru(NH_3)_5(py)]^{2+}$	—	—	1.5 × 10^7

* No k_3 contribution required in fit of data.

Other ruthenium(II) complexes $[Ru(en)_3]^{2+}$ (en = ethylenediamine) ($E^\ominus$ 0.21 V),[11] $[Ru(NH_3)_5(nicotinamide)]^{2+}$ and $[Ru(NH_3)_5(methyl\ nicotinate)]^{2+}$ ($E^\ominus$ values not known) also react rapidly and at the limit of the stopped-flow, which suggests that the mechanism is the same as for $[Ru(NH_3)_5(py)]^{2+}$.

DISCUSSION

Evidence in support of five- and four- (tetrahedral) co-ordinate forms of $[Cu^{II}L_2]^{2-}$ has been considered previously.[3] The mechanism (3)—(4) modified to include (5) appears to be an adequate description of the data now available. Thus two of the reductants $[Fe(CN)_6]^{4-}$ and $[Fe(edta)]^{2-}$ require (5) for an interpretation consistent with data for the milder reductants $[Fe(CN)_5(PPh_3)]^{3-}$ and $[Ru(NH_3)_5(pyz)]^{2+}$, which do not appear to have significant contributions from (5). With the stronger ruthenium(II) reductant $[Ru(NH_3)_5(py)]^{2+}$ k_3 seems to provide the dominant route.

The first four reductants could all conceivably react by an inner-sphere bridged activated complex, whereas $[Ru(NH_3)_5(py)]^{2+}$ must (because it is substitution inert and has no potential bridging ligands) react outer-sphere. For the first four complexes an alternative mechanism (7)—(8) involving the inner-sphere adduct Red,Cu^{II}

$$\text{Red} + Cu^{II} \overset{K}{\rightleftharpoons} \text{Red},Cu^{II} \qquad (7)$$

$$\text{Red},Cu^{II} \xrightarrow{k} \text{products} \qquad (8)$$

could account for the limiting kinetics. If this mechanism were applicable K would have a value 1.43×10^4 M^{-1} for the $[Fe(CN)_6]^{4-}$ reduction of $[CuL_2]^{2-}$.[3] Without special reasons such a large value would seem unlikely for two negative ions, and in any case would be expected to have other consequences. Further check experiments have confirmed that addition of $[Fe(CN)_6]^{3-}$ {10-fold excess over $[Fe(CN)_6]^{4-}$} does not affect (*i.e.* slow down) the reduction of $[CuL_2]^{2-}$. Nor does the ruthenium(III) product $[Ru(NH_3)_5(pyz)]^{3+}$ (four-fold excess) affect the rate of the $[Ru(NH_3)_5(pyz)]^{2+}$ reduction. In other words there is no evidence for favourable inner-sphere association of $[CuL_2]^{2-}$ with the oxidized form of the reductant whether this is a negatively or positively charged species. Moreover, stopped-flow $[Fe(CN)_6]^{4-}$ + $[CuL_2]^{2-}$ runs monitored at 900 nm (upper wavelength limit), in a search for intervalence bands in the near infrared region stemming from a binuclear adduct, gave no evidence for such absorbance. Perhaps most important of all, however, the kinetics with the copper(II) reactant in excess are consistent with (3)—(4) but not with (7)—(8).[3] Therefore the reaction scheme (3)—(4) with the elaboration in terms of (5) is favoured.

The pattern of k_1, k_2/k_{-1}, and k_3 rate constants in Table 3 for the first four entries seems perfectly self-consistent as already indicated. What is not clear is why $[Ru(NH_3)_5(py)]^{2+}$ should have the facility to outstrip by such a large margin the other reactants in terms of use of k_3. It is noted, Table 2, that while $[Ru(NH_3)_5(py)]^{2+}$ has a favourable $E^{\ominus}$ value, $[Fe(edta)]^{2-}$ is an even stronger reductant. A further possible rationale is therefore that step k_2 actually occurs by an inner-sphere process (without observable build-up of the inner-sphere adduct), and that this is a crucial factor in establishing the *Cu path (4). An outer-sphere reductant such as $[Ru(NH_3)_5(py)]^{2+}$ is then unable to utilize the k_2 path. As long as most of the Cu^{II} (say >95%) is present as the five-co-ordinate complex (as is required for the stationary-state approximation to apply), then k_{-1} cannot under any circumstances become the sole rate controlling process. Second-order behaviour (the k_3 path) is expected to be dominant therefore. Present information is that self-exchange rate constants (which are a measure of inherent electron-transfer capacity) are favourable in the case of the Fe^{II}–Fe^{III} couples,[12] and likely to be at least equally favourable in the case of the Ru^{II}–Ru^{III} reactions.[11,13] A perfectly reasonable possibility would be that other ruthenium(II) reductants $[Ru(en)_3]^{2+}$, $[Ru(NH_3)_5(\text{nicotinamide})]^{2+}$, and $[Ru(NH_3)_5(\text{methyl nicotinate})]^{2+}$ referred to also react outer-sphere.

We are grateful to the Swiss National Science Foundation for post-doctoral support (to P. L.), and the Kuwait Government for post-graduate support (to N. A-S.). Helpful discussions with Dr. A. G. Lappin are also acknowledged.

[1/1610 *Received, 15th October*, 1981]

REFERENCES

[1] H. Irving and D. H. Mellor, *J. Chem. Soc.*, 1952, 5222.

[2] B. R. James and R. J. P. Williams, *J. Chem. Soc.*, 1961, 2007.

[3] N. Al-Shatti, A. G. Lappin, and A. G. Sykes, *Inorg. Chem.*, 1981, **20**, 1466.

[4] H. L. Hodges, R. A. Holwerda, and H. B. Gray, *J. Am. Chem. Soc.*, 1974, **96**, 3132.

[5] D. J. Kenney, T. P. Flynn, and J. B. Gallini, *J. Inorg. Nucl. Chem.*, 1961, **20**, 75.

[6] R. Nast and K. W. Kruger, *Z. Anorg. Allg. Chem.*, 1965, **341**, 189.

[7] C. Creutz and H. Taube, *J. Am. Chem. Soc.*, 1973, **95**, 1086.

[8] L. Vogt, T. Katz, and S. Wiberley, *Inorg. Chem.*, 1965, **4**, 1157.

[9] G. Gaunder and H. Taube, *Inorg. Chem.*, 1970, **9**, 2627.

[10] D. M. Davies and D. H. Devia, *Chem. Br.*, 1981, **17**, 296.

[11] T. J. Meyer and H. Taube, *Inorg. Chem.*, 1968, **7**, 2369; H. Elsbernd and J. K. Beattie, *ibid.*, 1969, **8**, 893.

[12] R. Stasiw and R. G. Wilkins, *Inorg. Chem.*, 1969, **8**, 156.

[13] P. C. Ford, *Coord. Chem. Rev.*, 1970, **5**, 75.