Slow Electron Self-Exchange in Spite of a Small Inner-Sphere Reorganisation Energy − The Electron-Transfer Properties of a Copper Complex with a Tetradentate Bispidine Ligand

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The electron self-exchange rate of $[Cu(L)(OH_2)]^{2+/1+}$, k_{11}^{exp}(298.13 K) = 15 ± 11 $m^{-1}s^{-1}$ {L = dimethyl 3,7-dimethyl-9-oxo-2,4-bis(2-pyridyl)-3,7-diazabicyclo[3.3.1]nonane-1,5-dicarboxylate}, was determined by a cross reaction. The analysis, based on classical Marcus theory, indicates that this relatively slow rate is to a large extent due to enthalpic terms ($\Delta G_{11}^{\ddagger,exp}$ = 62.8 ± 3.5 kJ·mol^{-1}, $\Delta H_{11}^{\ddagger,exp}$ = 36.0 ± 2.7 kJ·mol^{-1} and $\Delta S_{11}^{\ddagger,exp}$ = –92 ± 10 J·mol^{-1}K^{-1}). The activation entropy is significant but not unusually large and the calculated outer-sphere reorganization energy, $\Delta G_{out}^{\ddagger,calc}$ = 20.5 kJ·mol^{-1}, is at least of the same order of magnitude as the calculated inner-sphere reorganisation energy $\Delta G_{in}^{\ddagger,calc}$ = 18.6 kJ·mol^{-1}, i.e. the deformation of the solvent sheath is a major reason for the slow electron transfer rate. This is believed to be due to the highly elastic coordination geometry which leads to little strain upon distortion enforced by the electron transfer but to comparably large structural changes and, hence, to a large outer-sphere reorganisation term.

Introduction

Transition metal complexes of bispidine-type ligands {Figure 1 shows the tetradentate ligand L = dimethyl 3,7-dimethyl-9-oxo-2,4-bis(2-pyridyl)-3,7-diazabicyclo[3.3.1]-nonane-1,5-dicarboxylate} have a number of unique properties: (i) Due to the comparably high degree of preorganisation and complementarity[1] they lead to very stable complexes (e.g., for Cu^{II} complexes, stabilities are in the same range as those with macrocyclic ligands[2−4]). (ii) L enforces a square pyramidal configuration upon Cu^{II} with a monodentate co-ligand in plane with two co-planar pyridines and a tertiary amine (N3), and with a tertiary amine (N7) as an apical donor.[4] This unique configuration for Cu^{II} leads to strong copper-substrate binding and interesting reactivities.[5−8] (iii) Most relevant for the present study is that while the bispidine ligands are rigid, the coordination sphere is elastic.[1] This follows from experimental structural data[9] and from empirical force field calculations[1,9−11] which indicate that metal ions of quite different sizes fit into the bispidine cavity without inducing much steric strain in the ligand, i.e. the structure of the ligand backbone is practically constant while the metal donor bonds vary in the expected ranges.[6,9] Another interesting observation based on experimental structural data and related to the elasticity of the coordination geometry is that there are various structurally different positions within the bispidine cavity.[9] For pentadentate derivatives of L we recently isolated and structurally characterised isomers along a Jahn−Teller-active vibrational mode.[12] Similar observations have also been made of a tetradentate derivative of L where the pyridine donors are 6-methyl-substituted.[10]

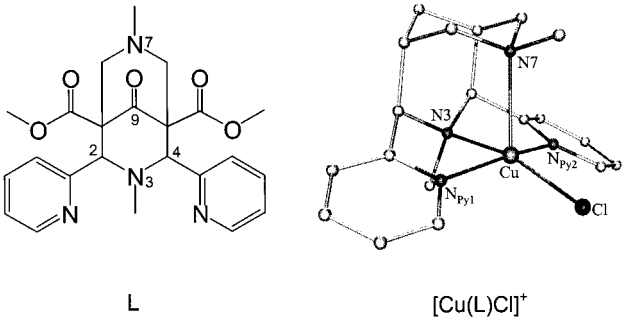

Figure 1. Diagram of the bispidine ligand L and a structural plot of the bispidine complex

The conclusion from all these observations is that the potential energy surface of metal-bispidine complexes is flat and has various shallow minima. Therefore, the inner-sphere reorganisation energy accompanying an electron self-exchange process should be small. Indeed, molecular-

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mechanics-derived potential energy surface scans of $[Cu^{I}(L)(X)]^{n+}$ and $[Cu^{II}(L)(X)]^{n+1}$ indicate that the inner-sphere reorganisation energy ΔG^{*}_{in} is around only 10−20 kJ·mol^{-1} (see Figure 2 and below). Does that mean that electron self-exchange is fast as, for example, in blue copper proteins?

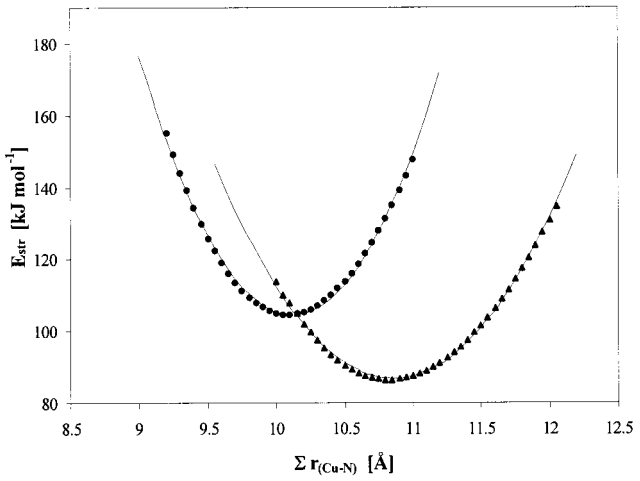

Figure 2. Potential energy scans for $[Cu^{II}(L)(NH_3)]^{2+}$ (filled circles) and $[Cu^{I}(L)(NH_3)]^{+}$ (filled triangles) (based on sum-constraints,[41] implemented with MOMEC97[42] and using a published parameterisation Scheme)[43]; the corresponding curves were obtained as least square fits to the equation $E = 0.5f(r - r_0)^2 + E_0$ (see below)

Results and Discussion

Experimentally Determined Electron Self-Exchange Parameters

Initial ^{1}H NMR line-broadening studies (CD_3CN, 298 K) indicated that electron self-exchange for the $[Cu^{II/I}(L)(NCCD_3)]^{2+/1+}$ couple is much slower than might have been expected (20 m^{-1}s^{-1} ≤ k_{11} ≤ 120 m^{-1}s^{-1}; see Supporting Information). Therefore, no accurate values are available from NMR titrations and the approximate range of the rate given here was only used as an estimate for the range of the electron self-exchange rate which was itself determined via a cross reaction using $[Co(sep)](NO_3)_2$ (sep = 1,3,6,8,10,13,16,19-octaazabicyclo[6.6.6]icosane) as a reducing agent [Equation (1), see Figure 3]. This was measured in water because the published electron self-exchange rate of the Co^{II} reductant has been obtained in aqueous solution (see below). Note that the change of solvent (CD_3CN, H_2O) implies that the two rates (NMR, cross reaction) are not directly comparable (different redox potential, different co-ligands and possible subtle changes in the mechanism). Indeed, there are examples where electron self-exchange rate constants of $Cu^{II/I}$ couples measured in H_2O and CH_3CN differ by as much as two orders of magnitude.[13] In other examples they are virtually identical.[14] Therefore, the only implication of the (inaccurate) rate of the NMR experiment is that electron self-exchange in the $[Cu^{II/I}(L)(solvent)]^{2+/1+}$ couple is slow.

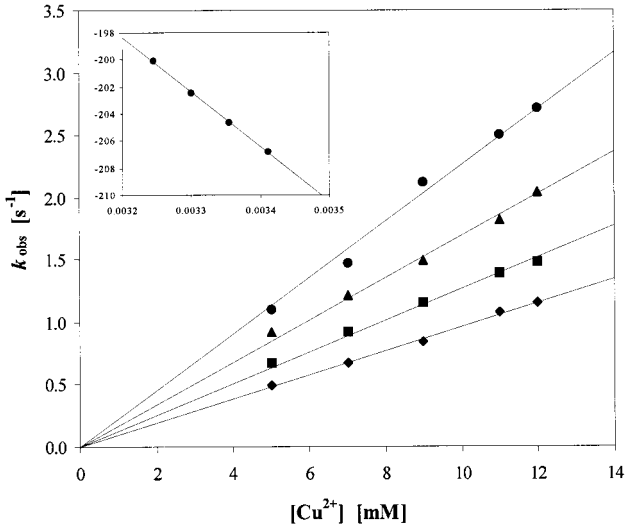

Figure 3. Plots of the pseudo-first-order rate constants k_{obs} for reaction (1) as a function of $[\{Cu^{II}(L)(OH_2)\}^{2+}]$ at 293.13 K (filled diamonds), 298.13 K (filled squares), 303.13 K (filled triangles) and 308.13 K (filled circles) in water (μ = 0.25 m, KNO_3), $[Co^{II}(sep)]_0$ = 5×10^{-4} m); inset: Eyring plot $[R\ln(k_{12}h/k_BT)$ [J·mol^{-1}·K^{-1}] vs. $1/T$ [K^{-1}]); k_{12} (298.13 K) = 126.9 ± 1.7 m^{-1}s^{-1}; $\Delta G^{\ddagger}_{12}$ (298.13 K) = 61.0 ± 1.2 kJ·mol^{-1}; $\Delta H^{\ddagger}_{12}$ = 40.3 ± 0.8 kJ·mol^{-1}; $\Delta S^{\ddagger}_{12}$ = −69.4 ± 2.8 J·mol^{-1}·K^{-1}

$$[Cu(L)(OH_2)]^{2+} + [Co(sep)]^{2+} \rightleftharpoons [Cu(L)(OH_2)]^{+} + [Co(sep)]^{3+} \quad (1)$$

The electron self-exchange rate, determined by the cross reaction, was obtained from the experimental data using the Marcus equations [Equation (2)−(6)[15,16] where Z is, as usual, 10^{11} m^{-1}s^{-1}]. The centre to centre distance in the precursor complex a_{ij} was obtained as the sum of the radii of the isolated complexes (a_j = $r([Co(sep)]^{3+/2+})$ = 4.5 ± 0.6 Å, identical to the published value.[17] a_i = $r([Cu(L)(NCCH_3)]^{2+/1+})$ = 6.3 ± 1.5 Å and both were calculated as $(a_x a_y a_z)^{1/3}$. The molecular dimensions along the three principal directional axes (a_x,a_y,a_z) were calculated using an established method.[16,18] The value K_{12} = 66.9 was derived from the redox potentials, measured under the same conditions as those used for the kinetic experiments [$E^0([Cu(L)(OH_2)]^{2+/1+})$ = −383 mV, $E^0([Co(sep)]^{3+/2+}$ = −491 mV, vs. Ag/AgCl]. The rate constant for the cross reaction k_{12} = 126.9 ± 1.7 m^{-1}s^{-1} was obtained from the experimental data (see Figure 3) and the electron self-exchange rate of the reductant is k_{22} = 5.1 ± 0.3 m^{-1} s^{-1}.[19] The self-exchange rate for the $[Cu^{I}(L)(OH_2)]^{+}$/$[Cu^{II}(L)(OH_2)]^{2+}$ couple is therefore k_{11} (298.13 K) = 15 ± 11 m^{-1}s^{-1},[20] i.e. as expected from the preliminary NMR experiments and a number of orders of magnitude slower than that of blue copper proteins which are in the range of

$k_{11} = 10^3-10^8$ $m^{-1}s^{-1}$ [21,22] and in the area of "slow" $Cu^{II/I}$ couples.[23−26]

$$k_{12} = \sqrt{k_{11}k_{22}K_{12}f_{12}}\ W_{12} \tag{2}$$

$$\ln f_{12} = \frac{1}{4}\frac{\left(\ln K_{12} + \frac{w_{12}-w_{21}}{RT}\right)^2}{\ln\frac{k_{11}k_{22}}{Z^2} + \frac{w_{11}+w_{22}}{RT}} \tag{3}$$

$$W_{12} = \exp\frac{-w_{12}-w_{21}+w_{11}+w_{22}}{2RT} \tag{4}$$

$$w_{ij} = \frac{z_i z_j e^2 N}{D_s a_{ij}\left(1+\beta a_{ij}\sqrt{\mu}\right)} \tag{5}$$

$$\text{with}\quad \beta = \sqrt{\frac{8\pi N e^2}{1000\, D_s k_B T}} \tag{6}$$

The activation parameters of the electron self-exchange reaction were determined by using Equations (7)−(10).[27] ΔS^0_{12} emerges from the reaction entropies of the redox couples [$\Delta S^0_{12} = \Delta S^0_{rc}(Cu^{II}) - \Delta S^0_{rc}(Co^{II})$,[28] $\Delta S^0_{rc}(Co^{II}) = 79.5$ $J\cdot mol^{-1}\cdot K^{-1}$,[29] $\Delta S^0_{rc}(Cu^{II}) = 130.3 \pm 1.8$ $J\cdot mol^{-1}\cdot K^{-1}$ (temperature dependence of the redox potential) i. e. $\Delta S^0_{12} = 50.8 \pm 1.8$ $J\cdot mol^{-1}\cdot K^{-1}$]. The activation parameters for the $[Co(sep)]^{3+/2+}$ self-exchange are from the literatures, i.e. $\Delta G^{\ddagger}_{22} = 68.8 \pm 3.2$ $kJ\cdot mol^{-1}$, $\Delta H^{\ddagger}_{22} = 40.2 \pm 2.1$ $kJ\cdot mol^{-1}$ and $\Delta S^{\ddagger}_{22} = -96 \pm 8$ $J\cdot mol^{-1}\cdot K^{-1}$ [19] and those for the cross reaction are $\Delta G^{\ddagger}_{12} = 61.0 \pm 1.2$ $kJ\cdot mol^{-1}$, $\Delta H^{\ddagger}_{12} = 40.3 \pm 0.8$ $kJ\cdot mol^{-1}$ and $\Delta S^{\ddagger}_{12} = -69.4 \pm 2.8$ $J\cdot mol^{-1}\cdot K^{-1}$, derived from the experiment (see Figure 3). The resultant experimental activation parameters for the $[Cu(L)(OH_2)]^{2+/1+}$ self-exchange are, therefore, $\Delta G^{\ddagger}_{11} = 62.8 \pm 3.5$ $kJ\cdot mol^{-1}$, $\Delta H^{\ddagger}_{11} = 36.0 \pm 2.7$ $kJ\cdot mol^{-1}$ and $\Delta S^{\ddagger}_{11} = -92 \pm 10$ $J\cdot mol^{-1}\cdot K^{-1}$.

$$\Delta G^{\ddagger}_{12} = \frac{\Delta G^{\ddagger}_{11}}{2} + \frac{\Delta G^{\ddagger}_{22}}{2} + \frac{\Delta G^{o}_{12}}{2}(1+\alpha) \tag{7}$$

$$\Delta S^{\ddagger}_{12} = \left(\frac{\Delta S^{\ddagger}_{11}}{2} + \frac{\Delta S^{\ddagger}_{22}}{2}\right)\left(1-4\alpha^2\right) + \frac{\Delta S^{o}_{12}}{2}(1+2\alpha) \tag{8}$$

$$\Delta H^{\ddagger}_{12} = \left(\frac{\Delta H^{\ddagger}_{11}}{2} + \frac{\Delta H^{\ddagger}_{22}}{2}\right)\left(1-4\alpha^2\right) + \frac{\Delta H^{o}_{12}}{2}(1+2\alpha) \tag{9}$$

$$\text{with}\quad \alpha = \frac{\Delta G^{o}_{12}}{4\left(\Delta G^{\ddagger}_{11} + \Delta G^{\ddagger}_{22}\right)} \tag{10}$$

Calculated Electron Self-Exchange Parameters

Three methods were used to calculate the inner-sphere reorganisation energy: (i) From the crossing point of the molecular-mechanics-derived energy surface scans [Figure 2, Equation (11)].[30] This method has some deficiencies and may only be considered as an upper limit.[25,31] (ii) From a free energy perturbation-type approach [Equation (12)], where $E^{*}_{str,Cu(I)}$ is the strain energy of the Cu^{II} structure, determined with the Cu^{I} force field and vice versa.[25] (iii) From the force constants of the Cu^{II} and Cu^{I} breathing modes, derived from the energy surface scans shown in Figure 2 (solid lines) and Equations 13−15[16] in which $n = 5$ is the number of donors and f_i is the averaged reduced force constant which approximately takes account of the asymmetry and rigidity of the ligand. The inner-sphere reorganisation energy, derived from the three approaches leads to similar values and these are, as expected, small: (i) $\Delta G^{*}_{in} = 18.6$ $kJ\cdot mol^{-1}$, (ii) $\Delta G^{*}_{in} = 13.4$ $kJ\cdot mol^{-1}$ and (iii) $\Delta G^{*}_{in} = 12.2$ $kJ\cdot mol^{-1}$. The three methods are based on the assumption that the Cu^{I} and Cu^{II} chromophores are similar, i.e. pentacoordinate. Published experimental data indicate that, as expected for Cu^{I}, there is a fast equilibrium between four- and five-coordinate structures (dissociation of one of the pyridine donors).[6,32] However, ^1H NMR spectra in D_2O indicate that the five-coordinate species is the major component in water and this is similar to earlier observations in acetonitrile.[6,32] Also, recent structural studies[33] indicate that, in addition to the published four- and five-coordinate Cu^{I} structures, there is a "pseudo-4-coordinate" Cu^{I} species with a short (2.0 Å) and a long (2.9 Å) $Cu-N_{pyridine}$ bond (pyridine lone-pair on the $Cu\cdots N_{py}$ axis) and a coordinated co-ligand ($NCCH_3$). This is also supported by DFT calculations[34] and is further evidence for the flat energy surface and validates the approximation of similar Cu^{I} and Cu^{II} chromophores. The three values for ΔG^{*}_{in} are all based on molecular mechanics calculations and, therefore, depend on the accuracy of the force field and on the model used (replacement of substituents at C1, C5, C9 of the bispidine backbone by hydrogen atoms, NH_3 instead of $NCCH_3$ as co-ligand; while chemically these changes might be unreasonable, in terms of the molecular mechanics model, which does not include any electronic effects, these are believed to be uncritical). The suitability of molecular mechanics for the computation of the inner-sphere reorganisation energy was therefore also confirmed by preliminary DFT calculations.[35]

$$\Delta G^{*}_{in} = 2E^{*}_{str} - E_{str,Cu(I)} - E_{str,Cu(II)} \tag{11}$$

The outer-sphere reorganisation energy can be obtained on the basis of a two-sphere (Equation 16) or an ellipsoid model (Equations 17−19).[16] The outer-sphere reorganisation energy, using the probably more accurate ellipsoid model, $\Delta G^{*}_{out,ellipsoid} = 20.5$ $kJ\cdot mol^{-1}$ ($\Delta G^{*}_{out,sphere} = 15.2$ $kJ\cdot mol^{-1}$) is of at least a similar magnitude to the inner-sphere reorganisation energy. The term derived from the

formation of the precursor complex (w_r = 2.80 ± 0.47 kJ·mol^{-1}) is significantly smaller.

$$\lambda_{in} = E^*_{str,Cu(I)} + E^*_{str,Cu(II)} - E_{str,Cu(I)} - E_{str,Cu(II)}$$

$$\Delta G^*_{in} = \frac{\lambda_{in}}{4} \quad (12)$$

$$\lambda_{in} = n\, f_i (\Delta a_0)^2 \quad (13)$$

$$\text{with} \quad f_i = \frac{2 f_{Cu(I)} f_{Cu(II)}}{f_{Cu(I)} + f_{Cu(II)}} \quad (14)$$

$$\text{and} \quad \Delta G^*_{in} = \frac{\lambda_{in}}{4} \quad (15)$$

$$\lambda_{out} = Ne^2 \left(\frac{1}{2a_1} + \frac{1}{2a_2} - \frac{1}{r} \right) \left(\frac{1}{D_{op}} - \frac{1}{D_s} \right) \quad (16)$$

$$\lambda_{out} = \frac{Ne^2 r^2}{2 I_a I_b^2} \left(\frac{1}{D_{op}} - \frac{1}{D_s} \right) S(\lambda_0) \quad (17)$$

$$\text{with} \quad S(\lambda_0) = \sum_{n=1,3,5\ldots}^{\infty} \frac{(2n+1)\lambda_0 (\lambda_0^2 - 1) Q_n(\lambda_0)}{P_n(\lambda_0)} \quad (18)$$

$$\text{and} \quad \lambda_0^2 = \frac{I_a^2}{I_a^2 - I_b^2} \quad (19)$$

The calculated rate, using the computed activation parameters, is k_{11}^{calc} = 4.5 10^3 m^{-1}s^{-1}, i.e. approx. 2 orders of magnitude too large (k_{11}^{obs} = 15 ± 11 m^{-1}s^{-1}, see above). An important point here is that the ΔG^* values in Equation (20) are not corrected for entropy effects. The inner-sphere reorganisation energy [Equation (11)] has been shown to have a linear dependence on the strain energies.[30] For a series of Co(III/II) hexamine couples this resulted in a $T\Delta S^*$ term (T = 298.13 K) of 20 kJ·mol^{-1}. This value is of a similar magnitude to the herein experimentally determined activation entropy at 298.13 K of $T\Delta S^{\ddagger}_{obs}$ = 27.4 kJ·mol^{-1}. With this 20 kJ·mol^{-1} added to ΔG^*_{calc} in Equation (21), k_{11}^{calc} = 1.5 m^{-1}s^{-1} is obtained which is in reasonable agreement with the experimentally determined self-exchange rate of k_{11}^{obs} (298.13 K) = 15 ± 11 m^{-1}s^{-1}. Note, however, that $\Delta S^{\ddagger}_{11}$ is the total transition state activation entropy and not the reorganisational entropy,[36] i.e. part of $\Delta S^{\ddagger}$ is included in the pre-exponential factor in the commonly used Equation (22) (which is a combination of Equations 20 and 21). Another possible reason for a reduction of Z (i.e. for a smaller value of the computed self-exchange rate) is reduced electronic coupling, i.e. nonadiabicity.

$$\Delta G^*_{calc} = w_r + \Delta G^*_{in} + \Delta G^*_{out} - RT \ln \frac{hZ}{k_B T} \quad (20)$$

$$k_{11}^{calc} = \frac{k_B T}{h} \exp \frac{-\Delta G^*}{RT} \quad (21)$$

$$k_{11}^{calc} = Z \exp\left(- \frac{w_r + \Delta G^*_{in} + \Delta G^*_{out}}{RT} \right) \quad (22)$$

Conclusions

As suggested by structural studies, the rearrangement of the coordination sphere of the copper-bispidine complex with L is a low energy process and ΔG^*_{in} = 18.6 kJ·mol^{-1} is overestimated rather than underestimated. Our analysis suggests that the experimentally determined slow electron self-exchange rate is to a large extent the result of a comparably high outer-sphere reorganisation energy barrier. A significant contribution to the activation entropy term and nonadiabicity might also be responsible for the relatively slow self-exchange rate. While our experimental and computational results do not yet allow a thorough and unambiguous assignment of the ratio of the various terms to the high activation barrier, it is clear that while the flat energy surface of transition metal bispidine complexes with L leads to a high elasticity and hence to a minimal loss of energy upon distortions enforced by the electron transfer, the elasticity also allows for large structural changes and this results in a significant perturbation of the solvation sheath (note that structural elasticity and solvation in small coordination compounds are both not directly comparable to those in proteins).[21,37,38] While this is a very specific result for the highly elastic Cu$^{II/I}$-bispidine system, the interesting but not unexpected general conclusion is that small inner-sphere reorganisation energies do not necessarily lead to fast electron transfer rates. This is in contrast to a common but naive interpretation of the Cu$^{II/I}$ electron self-exchange in blue copper proteins and a further argument in the discussion on entatic states.[39] Experiments and calculations which might help to answer some of the remaining questions, include kinetic studies with other bispidine derivatives and other bispidine redox couples (e.g., Co$^{III/II}$, Ru$^{III/II}$) and extensive DFT calculations. Some of these will be carried out in due course.

Experimental Section

Syntheses: Ligand L was synthesised as described in the literature.[40] The Cu^{II} complex as its triflate salt was obtained by addition of a hot solution of $Cu(CF_3SO_3)_2$ in dry CH_3CN to an equimolar suspension of L in dry CH_3CN. The resultant solution was stored in a diethyl ether diffusion bath to give $[Cu(L)(NCCH_3)(O\text{-}SO_2CF_3)]CF_3SO_3$ as deep blue crystals. $C_{27}H_{29}CuF_6N_5O_{11}S_2$ (841.22): calcd. C 38.55, H 3.47, N 8.33, S 7.62; found C 38.51, H 3.50, N 8.30, S 7.58. All solutions of the Cu^{II} complex were prepared with deionised and deoxygenated water and KNO_3 to keep

the ionic strength at 0.25 m. The Cu^{I} complex was obtained as described previously.[32]

$[Co(sep)]Cl_3$ (Aldrich) was converted into its nitrate salt by treatment of an aqueous solution of 1 equivalent of $[Co(sep)]Cl_3$ with 3 equivalents of $AgNO_3$. After filtration, solid KNO_3 was added slowly to the filtrate until precipitation of the orange $[Co(sep)](NO_3)_3$ was complete. This was recrystallised from a small amount of warm water and the precipitate was dried in vacuo. A solution of $[Co(sep)](NO_3)_3$ of the appropriate concentration and desired ionic strength (0.25 m, KNO_3) in deionised and deoxygenated water was then treated with an excess of zinc dust under Ar until the complex was fully reduced (approx. 4 h, colourless solution). The solution was used for kinetic measurements within 3 h after preparation.

Measurements: Redox potentials were measured by cyclic voltammetry using a BAS-100B electrochemical analyser with a scan rate of 100 mV/s. The electrode setup consisted of a glassy/carbon working electrode, a platinum auxiliary electrode and an aqueous Ag/AgCl reference electrode. The concentrations of the solutions were 10^{-3} m for the $Co^{III/II}$(sep) couple and 10^{-2} m for the $Cu^{II/I}$(L) couple, μ = 0.25 m (KNO_3). The temperature of the solutionswas maintained using a circulating water bath (Haake K 20).

^{1}H NMR Spectra: (60 mm $[Cu^{I}(L)]$, 0−28 mm $[Cu^{II}(L)]$, CD_3CN, T = 193 K) were obtained on a Bruker AS 300 spectrometer (300.13 MHz). Chemical shifts (δ, ppm) are relative to the solvent. Note that in addition to the electron self-exchange there is a dynamic process between two different structures of $[Cu^{I}(L)(NCCD_3)]^+$ (four- and five-coordinate).[6,32] ^{1}H NMR spectroscopy suggests that this process is much faster than the electron self-exchange reaction and that the five-coordinate complex is the major species in solution. This also emerges for the corresponding aqua complexes measured in aqueous solution and it is in agreement with preliminary DFT calculations.[34]

Kinetics: Measurements were performed on an Applied Photophysics SX.18MV-R stopped-flow spectrophotometer. The temperatures of the solutions were maintained (± 0.1 °C) using a circulating water bath (Haake K20). The cross reactions were carried out under pseudo-first-order conditions (Cu^{II} in at least 10-fold excess) and the rates were monitored at 474 nm. The kinetic data were analysed using the !SX.18MV Kinetic Spectrometer Workstation Software v4.46.

Supporting Information: Details of the determination of $K_{Cu\text{-}Cl}$, the NMR line-broadening studies, the experimentally measured entropy of the redox potential and the calculations of the electron transfer rates are given as Supporting Information (see also footnote on the first page of this article)

Acknowledgments

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