# Thermodynamics of Redox Processes and Kinetics and Mechanism of Electron Self-Exchange Reactions in the Bis(*N*,*N*-diethyldithiocarbamato)copper(II)/Iodine/Dichloromethane System

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The thermodynamics of complex formation between $Et_4NI$ and $I_2$ in $CH_2Cl_2$ and the redox processes in the bis(*N*,*N*-diethyldithiocarbamato)copper(II) $[Cu^{II}L_2]/I_2/CH_2Cl_2$ system have been studied spectrophotometrically. The reversibility of the reactions of formation of copper(III) complexes was established and their thermodynamic parameters determined: $Cu^{II}L_2 + {}^3/_2I_2 \rightleftarrows [Cu^{III}L_2]I_3$ {log$K$ = 5.80 (298 K), $\Delta H$ = –35.0 kJ·mol$^{-1}$, and $\Delta S$ = –6.7 J·K$^{-1}$·mol$^{-1}$} and $[Cu^{III}L_2]I_3 + I_2 \rightleftarrows [Cu^{III}L_2]I_5$ {log$K$ = 2.02 (298 K), $\Delta H$ = –11.1 kJ·mol$^{-1}$, and $\Delta S$ = 1.3 J·K$^{-1}$·mol$^{-1}$}. The rate constants and activation parameters for the electron self-exchange reactions between $Cu^{II}L_2$ and $[Cu^{III}L_2]I_n$ ($n$ = 3, 5) in the $CD_2Cl_2$ solutions were determined by NMR line-broadening of the ligand L protons: $k_e = 3.0 \cdot 10^8$ M$^{-1}$·s$^{-1}$ (298 K), $\Delta H^{\neq}$ = 6.1 kJ·mol$^{-1}$, and $\Delta S^{\neq}$ = –62.3 J·K$^{-1}$ mol$^{-1}$. To account for the kinetic parameters, an unusual mechanism for the self-exchange reaction was suggested. This mechanism involves the prior formation of the $Cu^{II}L_2I_nCu^{III}L_2$ intermediate, in which considerable delocalization of electron density through the orbitals of copper and bridging iodine atoms is achieved, followed by electron transfer. The formation of the intermediate was supported by ESR data and quantitative analysis of the activation parameters with the use of quantum chemical computations by the DFT method at the B3LYP/3-21G* level.

## Introduction

The study of redox reactions of $Cu^I$, $Cu^{II}$, and $Cu^{III}$ complexes with sulfur-containing ligands is of interest for fundamental understanding of electron-transfer mechanisms. In this regard, the interconversions of copper(II) and copper(III) dithiocarbamates deserve particular attention. The electrochemical oxidation of the copper(II) dithiocarbamates to copper(III) is a reversible process at a platinum electrode.[1] With a "soft" oxidative agent such as iodine, one would also expect a reversible copper(II)/copper(III) transformation in solution. This would in principle allow one to evaluate both the thermodynamic parameters of the redox processes and the kinetic characteristics of the copper(II)/copper(III) electron self-exchange reactions. A first attempt to turn these possibilities into reality has been undertaken in this work.

We have investigated the thermodynamics of the redox processes and kinetics of the electron self-exchange reactions in the bis(*N*,*N*-diethyldithiocarbamato)copper(II) $[Cu^{II}L_2]/I_2/CH_2Cl_2$ ($CD_2Cl_2$) system by means of spectrophotometric, NMR, and ESR methods. Moreover, for the characterization of polyiodide anions forming in these solutions, the thermodynamics of complex formation in the $Et_4NI/I_2/CH_2Cl_2$ system have been studied spectrophotometrically.

Previously,[1–5] treatment of copper(II) *N*,*N*-dialkyldithiocarbamates ($Cu^{II}L'_2$) with iodine had resulted in the isolation of copper(III) complexes of compositions $[Cu^{III}L'_2]I_3$[1–5] and $[Cu^{III}L'_2]I_5$[4] as crystals. Two of these, $[Cu^{III}(S_2CNnBu_2)_2]I_3$ and $[Cu^{III}(S_2CNEt_2)_2]I_3$, have been characterized by X-ray data.[3,5] No thermodynamic or kinetic parameters of reactions of this type have been reported in the literature.

To the best of our knowledge, the only directly studied copper(II)/copper(III) electron self-exchange reaction was the electron transfer between the copper complexes with the deprotonated tripeptide tris-α-aminoisobutyrate $[Aib_3H_{(-2)}{}^{3-}]$ in aqueous medium.[6] Those authors[6] had suggested an outer-sphere electron exchange mechanism, but not ruled out bridging by an axially bound water molecule. In this investigation we have attempted to elucidate the mechanism of the electron self-exchange reaction between the copper(II) and copper(III) dithiocarbamates.

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## Results and Discussion

### Thermodynamics of Complex Formation and Redox Processes

For interpretation of the experimental data in the $Cu^{II}L_2/I_2/CH_2Cl_2$ system, previous investigations of complex formation between $Et_4NI$ and $I_2$ in $CH_2Cl_2$ are of considerable significance. The $I_2$ concentration-dependence of the molar absorption coefficient (ε) of $Et_4NI$ in $CH_2Cl_2$ solutions (Figure 1) is adequately computer-simulated by two equilibria with consecutive addition of two $I_2$ molecules to $Et_4NI$, but the first equilibrium constant ($K_1$) cannot be exactly estimated at these concentration conditions. The $K_1$ values were therefore deduced from the dependence of the molar absorption coefficient of the $I_2$ solution ($c_{I_2} = 2 \cdot 10^{-5}$ M) upon the $Et_4NI$ concentration ($2 \cdot 10^{-6}$ to $8 \cdot 10^{-5}$ M) at λ 365 nm (Table S1, Supporting Information), and these values were then fixed at computations of the addition constant of $I_2$ to $Et_4NI_3$ ($K_2$) from the above-mentioned $\varepsilon - c_{I_2}$ dependence at λ 400 nm (Table S2). The enthalpy ($\Delta H$) and entropy ($\Delta S$) of each equilibrium were calculated from the log $K_{1,2}$ magnitudes at different temperatures. The derived $\log K_{1,2}$, $\Delta H_{1,2}$, and $\Delta S_{1,2}$ parameters are given in Table 1. With the aid of the computed mol fractions of the $Et_4NI_3$ and $Et_4NI_5$ compounds their electronic absorption spectra were reconstructed (Figure 2).

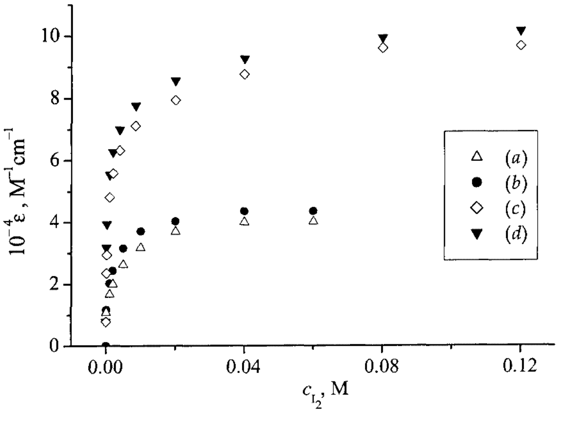

Figure 1. Dependence of the molar absorption coefficient (ε) upon the $I_2$ concentration in the systems $Et_4NI/I_2/CH_2Cl_2$ (*a*, *b*) and $Cu^{II}L_2/I_2/CH_2Cl_2$ (*c*, *d*) at 298 K (*a*, *c*) and 278 K (*b*, *d*), $c_{CuL_2} = 1 \cdot 10^{-4}$ M (*a*, *b*), $c_{Et_4NI} = 6.25 \cdot 10^{-5}$ M (*c*, *d*); λ = 400 nm

Table 1. Thermodynamic parameters of equilibria in the systems $Et_4NI/I_2/CH_2Cl_2$ and $Cu^{II}L_2/I_2/CH_2Cl_2$

| Equilibrium | log*K* (298 K) | $\Delta H$ [kJ·mol$^{-1}$] | $\Delta S$ [J·K$^{-1}$·mol$^{-1}$] |
|---|---|---|---|
| $Et_4NI + I_2 \rightleftarrows Et_4NI_3$ | 7.20±0.10 | −60.0±4.4 | −63.6±15.1 |
| $Et_4NI_3 + I_2 \rightleftarrows Et_4NI_5$ | 2.33±0.03 | −16.8±1.0 | −11.6±3.4 |
| $Cu^{II}L_2 + 3/2I_2 \rightleftarrows [Cu^{III}L_2]I_3$ | 5.80±0.04 | −35.0±1.3 | −6.7±4.6 |
| $[Cu^{III}L_2]I_3 + I_2 \rightleftarrows [Cu^{III}L_2]I_5$ | 2.02±0.06 | −11.1±1.0 | 1.3±3.5 |

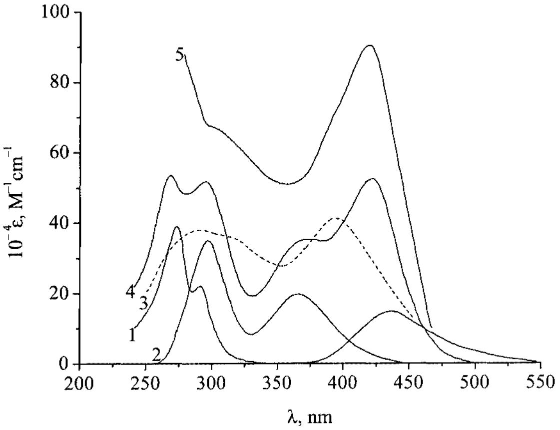

Figure 2. Electronic absorption spectra of $Cu^{II}L_2$ (1), $Et_4NI_3$ (2), $Et_4NI_5$ (3), $[Cu^{III}L_2]I_3$ (4), and $[Cu^{III}L_2]I_5$ (5) in $CH_2Cl_2$ at 298 K

Two absorption bands of the $I_3^-$ spectrum in $CH_2Cl_2$ have the parameters $\lambda_{max}$ 363 nm ($\varepsilon_{max}$ $2.5 \cdot 10^4$ M$^{-1}$·cm$^{-1}$) and $\lambda_{max}$ 293 nm ($\varepsilon_{max}$ $4.3 \cdot 10^4$ M$^{-1}$·cm$^{-1}$), which are essentially coincident with those reported for triiodide anion in $CH_2Cl_2$,[7] acetonitrile, and 1,2-dichlorethane[8] and somewhat different from those found for $I_3^-$ in water.[9,10] These two bands correspond[7,11–13] to the allowed singlet-singlet transitions $\pi_g \rightarrow \sigma_u^*$ and $\sigma_g \rightarrow \sigma_u^*$, respectively, for the linear $I_3^-$ anion with nominal $D_{\infty h}$ symmetry (in theoretical studies this symmetry is predicted for the gas phase[11–17] but it can be slightly broken by solvation[18,19]).

The $I_5^-$ spectrum in $CH_2Cl_2$ exhibits bands at $\lambda_{max}$ 392 nm ($\varepsilon_{max}$ $5.0 \cdot 10^4$ M$^{-1}$·cm$^{-1}$) and $\lambda_{max}$ 288 nm ($\varepsilon_{max}$ $4.6 \cdot 10^4$ M$^{-1}$·cm$^{-1}$) with a "shoulder" at $\lambda_{sh}$ 312 nm ($\varepsilon_{sh}$ $4.4 \cdot 10^4$ M$^{-1}$·cm$^{-1}$); these differ from those in acetonitrile ($\lambda_{max}$ 390 nm, $\varepsilon_{max}$ $2.5 \cdot 10^4$ M$^{-1}$·cm$^{-1}$; $\lambda_{max}$ 310 nm, $\varepsilon_{max}$ $2.1 \cdot 10^4$ M$^{-1}$·cm$^{-1}$)[20] and in *tert*-butyl alcohol ($\lambda_{max}$ 395 nm, $\varepsilon_{max}$ $3.1 \cdot 10^4$ M$^{-1}$·cm$^{-1}$; $\lambda_{max}$ 315 nm, $\varepsilon_{max}$ $2.5 \cdot 10^4$·M$^{-1}$ cm$^{-1}$).[20] In solid compounds, the $I_5^-$ anion exhibits either a bent structure (symmetry $C_{2v}$)[12,21–23] or a linear structure (symmetry $D_{\infty h}$).[24–28] According to calculations,[15,29] however, interconversions between these $I_5^-$ conformations under vacuum require little or no energy expenditure. In our opinion the band at 392 nm (25510 cm$^{-1}$) in the $I_5^-$ spectrum can be assigned to the allowed $4\sigma_u \rightarrow 5\sigma_g^*$ transition for the $D_{\infty h}$ symmetry or the $6b_1 \rightarrow 8a_1^*$ transition for the $C_{2v}$ symmetry (see notations in ref.[15]) and the band at 288 nm (34720 cm$^{-1}$) and the "shoulder" at $\lambda_{sh}$ 312 nm (32050 cm$^{-1}$) are attributable to the allowed transitions $3\pi_u \rightarrow 5\sigma_g^*$ ($D_{\infty h}$ symmetry) and $3b_2 \rightarrow 8a_1^*$ ($C_{2v}$ symmetry), respectively. This assignment is in good accordance with the theoretically calculated difference between the $4\sigma_u$ and $3\pi_u$ orbital energies (9130 cm$^{-1}$)[15] or between the $6b_1$ and $3b_2$ orbital energies (7290 cm$^{-1}$).[15]

The $\log K_1$ value obtained (Table 1) is very similar to the reported values of $\log K_1$ in nitromethane (6.7[30] and 7.4[31] at 293 K), nitrobenzene (8.0),[32] sulfolane (7.4),[33] ethylene carbonate (6.6 at 313 K),[34] propylene carbonate (7.9),[35] acetonitrile (6.6,[30] 7.0,[31] 7.4,[36] 6.85,[37] 6.75,[38] and

6.80[39]), dimethylacetamide (7.4),[39] DMF (7.0),[39] and DMSO (6.9),[39] while differing fundamentally from the $\log K_1$ values in methanol (4.94[38] and 4.30[39]), ethanol (4.13[38] and 4.70[38]), and water (2.85,[9] 2.86,[10] and 2.84[38]). The $\log K_2$ value found (Table 1) is fairly close to the $\log K_2$ values in nitrobenzene (2.7),[32] ethylene carbonate (1.8 at 313 K),[34] propylene carbonate (1.9),[35] acetonitrile (2.0−2.3),[20] and *tert*-butyl alcohol (2.03)[20] (the data for water are contradictory: $\log K_2 = 0.95$[40] or 2.3[41]). As is evident from Table 1, the difference between $\log K_1$ and $\log K_2$ is mainly the result of the enthalpy constituent. This also governs the decrease in $\log K_1$ on going from $CH_2Cl_2$ to $H_2O$ ($\Delta H_1 = -21.3$[9] or $-19.9$[10,40] kJ·mol$^{-1}$). The more positive $\Delta S_2$ value relative to $\Delta S_1$ (Table 1) accounts for the rigid $I_3^-$ structure and the flexible $I_5^-$ structure with interconversions between the bent and linear $I_5^-$ conformers,[15,29] as mentioned above.

Let us consider the $Cu^{II}L_2/I_2/CH_2Cl_2$ system. The excellently reproducible dependence of the molar absorption coefficient of the $Cu^{II}L_2$ solutions on the $I_2$ concentration can be computer-simulated equally well by two alternative equilibrium models involving formation of the following pairs of complexes: 1) $[Cu^{III}L_2]I$ and $[Cu^{III}L_2]I_3$, or 2) $[Cu^{III}L_2]I_3$ and $[Cu^{III}L_2]I_5$ (Table S3). The electronic absorption spectra were reconstructed for each pair of complexes on the basis of their respective calculated equilibrium constants, and these pointed unambiguously to the suitability of the second model only. Indeed, the reconstructed spectra of $[Cu^{III}L_2]I_3$ and $[Cu^{III}L_2]I_5$ (Figure 2) are superpositions of the $I_3^-$ and $I_5^-$ spectra discussed above and the spectrum of the $[Cu^{III}L_2]^+$ cation produced by the electrochemical oxidation of $Cu^{II}L_2$.[1] Note that the asymmetric band at $\lambda_{max}$ 435 nm for $Cu^{II}L_2$ (Figure 2) is attributable to the composition of two ligand-to-metal charge-transfer transitions,[42,43] $\pi S \rightarrow 3d_{x^2-y^2}$ (two bands with $\lambda_{max}$ 270 and 290 nm in the $Cu^{II}L_2$ spectra (Figure 2) correspond to pure ligand $\pi \rightarrow \pi^*$ transitions).[43] By analogy, the band at $\lambda_{max}$ 418 nm for $[Cu^{III}L_2]^+$ (Figure 2) can be assigned to the $\pi S \rightarrow 3d_{x^2-y^2}$ transitions. Thus, according to the spectrophotometric data, the following equilibria operate in the $Cu^{II}L_2/I_2/CH_2Cl_2$ system:

$$Cu^{II}L_2 + 3/2I_2 \underset{}{\overset{K_3}{\rightleftharpoons}} [Cu^{III}L_2]I_3 \quad (1)$$

$$[Cu^{III}L_2]I_3 + I_2 \overset{K_4}{\rightleftharpoons} [Cu^{III}L_2]I_5 \quad (2)$$

The validity of reactions according to Equations (1) and (2) was supported by the isolation of $[Cu^{III}L_2]I_3$ and $[Cu^{III}L_2]I_5$ crystals under suitable concentration conditions (see Exp. Sect.). The reversibility of process (2) is apparent from its similarity to the $Et_4NI_5$ formation reaction described above. The reversibility of process (1) was established by ESR in the following manner. Dissolution of the diamagnetic $[Cu^{III}L_2]I_3$ crystals in $CH_2Cl_2$ ($c_{Cu} = 1\cdot10^{-3}$ M) gives rise to the ESR spectrum with the spin-Hamiltonian parameters $g_o = 2.048 \pm 0.001$ and $A_o = (75.8 \pm 0.5)\cdot10^{-4}$ cm$^{-1}$ (298 K), which correspond to the $Cu^{II}L_2$ complex. The integral intensity of the ESR signals of the $[Cu^{III}L_2]I_3$ solution in question is 25(±3)% of that for the $Cu^{II}L_2$ solution at the same concentration ($1\cdot10^{-3}$ M). This value is nearly equal to the $Cu^{II}L_2$ fraction (22.1%) calculated for the $[Cu^{III}L_2]I_3$ dissociation from the obtained $K_3$ and $K_4$ constants. This leftward shift of equilibrium (1) is suppressed by introduction of iodine into the $Cu^{II}L_2$ solution: at $c_{I_2} = 0.1$ M the ESR spectrum disappeared entirely.

The equilibrium constants of Equations (1) and (2) and the thermodynamic parameters computed from the temperature-dependence of $\log K_3$ and $\log K_4$ are listed in Table 1. The $\log K_3$ constant can be presented as a sum of three contributions [Equation (3)]

$$\log K_3 = -\frac{\Delta G_3^{\,0}}{2.3RT} = \frac{nF}{2.3RT}\cdot\Delta E^0 + \log K_{M^+I^-} + \log K_{MI_3} \quad (3)$$

where $\Delta G_3^0$ is the standard free energy of the reaction (1), $\Delta E^0$ is the standard electromotive force[44] of the reaction $Cu^{II}L_2 + {}^1/_2I_2 \rightleftharpoons [Cu^{III}L_2]^+ + I^-$, $K_{M^+I^-}$ is the constant of the association process $[Cu^{III}L_2]^+ + I^- \rightleftharpoons [Cu^{III}L_2]I$, and $K_{MI_3}$ is the constant of the equilibrium $[Cu^{III}L_2]I + I_2 \rightleftharpoons [Cu^{III}L_2]I_3$. With the requirement that replacement of $M^+ = [Cu^{III}L_2]^+$ by $M^+ = Et_4N^+$ has little or no effect on the constants above, it is possible to take $\log K_{MI_3} = K_1 = 7.20$ and $\log K_{M^+I^-} = 4.9$.[44] With these values and $\log K_3 = 5.80$ (Table 1), according to Equation (3), a value of $\Delta E^0 = -0.375$ V (298 K) would be estimated. The $\Delta E^0$ value in $CH_2Cl_2$ has not been determined by electrochemical methods, but the $\Delta E^0$ value obtained above is reasonably close to the difference between the normal electrode potential for the reaction ${}^1/_2I_2 + e^- \rightarrow I^-$ (0.36 V in acetone)[30] and the half-wave potential for the oxidation process $Cu^{II}L_2 \rightleftharpoons [Cu^{III}L_2]^+ + e^-$ (0.70 V in acetone).[1] Thus, the spontaneous course of reaction (2) in dichloromethane is provided by the energy-favorable processes of triiodide anion formation and ionic association.

The thermodynamic description achieved for the $Cu^{II}L_2/I_2/CH_2Cl_2$ system allows one to regulate the $Cu^{II}$ and $Cu^{III}$ contents by varying the $I_2$ concentration and to study the kinetics of electron self-exchange reactions between the complexes $Cu^{II}L_2$ and $[Cu^{III}L_2]I_n$ ($n$ = 3, 5) at different temperatures on this basis.

## Kinetics of Electron Self-exchange

$^1H$ NMR spectra of the $Cu^{II}L_2$ solutions in $CD_2Cl_2$ display only the signal of the methyl protons of the coordinated L ligand, with the chemical shift (δ) varying from 0.36 to 0.67 ppm and the line-width ($\Delta\nu_{1/2}$) decreasing from 86 to 46 Hz as the temperature increases from 248 to 298 K; the $^1H$ NMR signal of the L methylene protons is so broad that it defies observation. As iodine is added to the $Cu^{II}L_2$ solution ($c_{I_2} \leq 1\cdot10^{-3}$ M), the NMR signal of the $CH_3$-protons is progressively narrowed and shifted to low field (the signal of the $CH_2$-protons remains unobservable). Such a situation corresponds to a "fast exchange"[45] of the L methyl protons between two different environments **A** (diamagnetic $[Cu^{III}L_2]I_n$) and **B** (paramagnetic $Cu^{II}L_2$) through electron self-exchange. On a further increase in the $I_2$ concentration (above $1 \cdot 10^{-2}$ M), multiplet structures of the $^1H$ NMR signals appear for both methyl and methylene protons, and their chemical shifts cease to be changed and range up to 1.41−1.43 and 3.81−3.85 ppm, respectively. In the $I_2$ concentration interval from 0.03 to 0.12 M, with decreasing $I_2$ content (and correspondingly increasing $Cu^{II}L_2$ fraction), the line-widths of the methyl triplet are essentially unaffected, while the lines of the methylene quadruplet are significantly broadened. The line-widths of the $CH_3$-protons decrease and those of the $CH_2$-protons increase with increasing temperature from 268 to 298 K (Figure 3). All these facts clearly attest to the "fast exchange" limiting case being reached for the methyl protons and the "slow exchange" limiting case for the methylene protons (see ref.[45]).

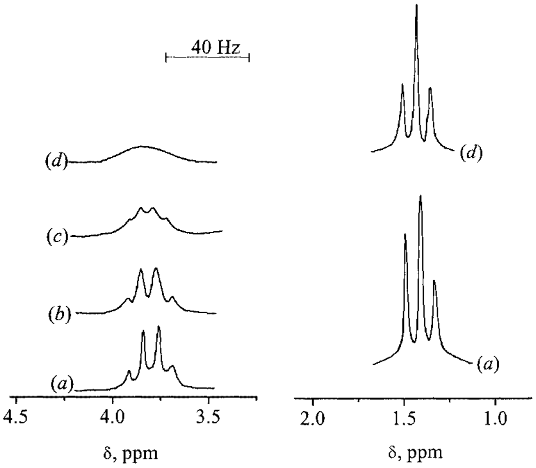

Figure 3. $^1H$ NMR spectra of the $Cu^{II}L_2$ solutions in $CD_2Cl_2$ with $I_2$ (0.04 M) at 268 K (*a*), 278 K (*b*), 288 K (*c*), and 298 K (*d*); $c_{CuL_2} = 1.5 \cdot 10^{-3}$ M

Under conditions suitable for the quantitative kinetic experiments ($c_{I_2} = 0.03-0.12$ M and $T = 268-298$ K) the mol fractions ($P$) calculated from the $K_3$ and $K_4$ constants change from $3.7 \cdot 10^{-7}$ to $5.0 \cdot 10^{-5}$ for $Cu^{II}L_2$, from 0.048 to 0.238 for $[Cu^{III}L_2]I_3$, and from 0.952 to 0.762 for $[Cu^{III}L_2]I_5$. Consequently, the condition $[\mathbf{A}] >> [\mathbf{B}]$ is obeyed, and with this the exchange between **A** ($[Cu^{III}L_2]I_n$) and **B** ($Cu^{II}L_2$) is described by the Swift−Connick equation,[46] which at $\Delta\omega_{AB} \approx 0$ is reduced to relation (4)

$$\pi\Delta\nu_{1/2} = \frac{1}{T_2} = \frac{1}{T_{2A}} + \frac{P_B}{T_{2B} + \tau_B} \qquad (4)$$

where $P_B$ is the mol fraction of $Cu^{II}L_2$, $T_{2A}$ and $T_{2B}$ denote the transverse relaxation times of the protons in the dia- and paramagnetic positions, respectively, and $\tau_B$ is the lifetime of the protons in the latter position. Equation (4) holds for the bimolecular electron self-exchange reaction according to Equation (5)

$$Cu^{II}L_2 + [^*Cu^{III}L_2]I_n \xrightleftharpoons{k_e} [Cu^{III}L_2]I_n + {}^*Cu^{II}L_2 \quad (n = 3, 5) \qquad (5)$$

under the condition that the chemical shifts of the **A** form, the $T_{2A}$ relaxation times, and the electron self-exchange rate constants ($k_e$) are independent on the size of the $I_n^-$ counter-ion ($n$ = 3, 5) with $\tau_B^{-1} = k_e[Cu^{III}L_2I_n]$ in this case. From the above values of $P_B$ and $\Delta\nu_{1/2} = (\pi \cdot T_{2B}^{CH_3})^{-1}$ for the $CH_3$-protons in $Cu^{II}L_2$ it follows that at $c_{I_2} = 0.03-0.12$ M the contribution of the last term in Equation (4) to the methyl proton line-widths is negligibly small (< 0.01 Hz). Because of this, for the "slow exchange" of the L methylene protons ($T_{2B}^{CH_2} << \tau_B$), the difference of the NMR line-widths of the $CH_2$- and $CH_3$-protons ($\Delta\Delta\nu_{1/2}$) can be represented by Equation (6) {with $P_B[Cu^{III}L_2I_n] = [Cu^{II}L_2]$}

$$\pi\Delta\Delta\nu_{1/2} = \pi\left(\Delta\nu_{1/2}^{CH_2} - \Delta\nu_{1/2}^{CH_3}\right) = \left(\frac{1}{T_{2A}^{CH_2}} - \frac{1}{T_{2A}^{CH_3}}\right) + k_e\left[Cu^{II}L_2\right] \qquad (6)$$

The application of the $\pi\Delta\Delta\nu_{1/2}$ parameter has the advantage that this enables one to eliminate almost fully the $\Delta\nu_{1/2}^{CH_2}$ contributions from the variation of the solution viscosity, the magnetic field inhomogeneity, the signal acquisition regime, and so on as $T_{2A}^{CH_2} << T_{2A}^{CH_3}$. As Figure 4 suggests, plots of the $\pi\Delta\Delta\nu_{1/2}$ parameter as a function of $[Cu^{II}L_2]$ are linear, with small intercepts. Therefore, all discussed conditions for the use of Equation (6) are fulfilled. True, it should be pointed out that the $k_e$ constant accounts mainly for the $Cu^{II}L_2/[Cu^{III}L_2]I_5$ exchange because of a predominance of the last form at the kinetic experiment conditions (Table S4). (The experimental relationship $T_{2B}^{CH_2} << T_{2B}^{CH_3}$, as used above, can reasonably be explained in terms of a dipole−dipole mechanism of the proton relaxation[45] by virtue of a greater distance from the paramagnetic center for the methyl protons of L than for the methylene protons). From the $k_e$ constants derived by Equation (6) at different temperatures (Table S4), the activation enthalpy ($\Delta H^{\neq}$) and entropy ($\Delta S^{\neq}$) of the electron self-exchange reaction were determined by application of the Eyring equation. The obtained values of $k_e$, $\Delta H^{\neq}$, and

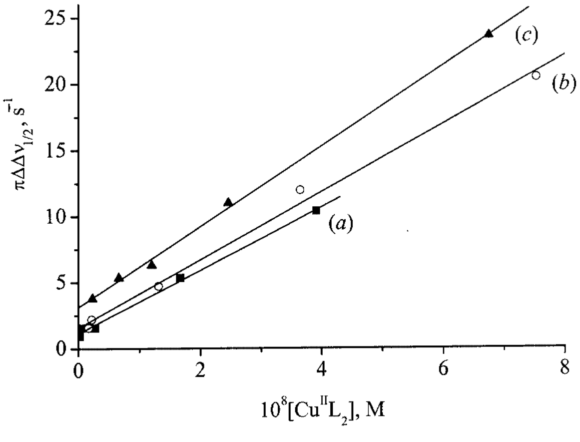

Figure 4. Dependence of the $\pi\Delta\Delta\nu_{1/2}$ parameter on $[Cu^{II}L_2]$ in the $Cu^{II}L_2/I_2/CD_2Cl_2$ system at 278 K (*a*), 288 K (*b*), and 298 K (*c*)

Table 2. Rate constants and activation parameters of the electron self-exchange reaction in the $CD_2Cl_2$ solution

$$Cu^{II}L_2 + [^{*}Cu^{III}L_2]I_n \xrightleftharpoons{k_e} [Cu^{III}L_2]I_n + {}^{*}Cu^{II}L_2 \quad (n = 3, 5)$$

| $T$, K | $k_e$ [$M^{-1}$ $s^{-1}$] | |
|---|---|---|
| 268 | $(2.04\pm0.21)\cdot10^8$ | |
| 278 | $(2.38\pm0.09)\cdot10^8$ | $\Delta H^{\neq} = 6.1\pm0.9$ kJ·mol$^{-1}$ |
| 288 | $(2.57\pm0.09)\cdot10^8$ | $\Delta S^{\neq} = -62.3\pm3.0$ J·K$^{-1}$·mol$^{-1}$ |
| 298 | $(3.04\pm0.07)\cdot10^8$ | |

$\Delta S^{\neq}$ are listed in Table 2 and are essentially different from those found for the related electron self-exchange reaction between the copper(II) and copper(III) complexes (with tris-α-aminoisobutyrate as a ligand) in aqueous medium ($k_e = (5.5\pm0.1)\cdot10^4$ $M^{-1}\cdot s^{-1}$ (298 K), $\Delta H^{\neq} = 29\pm2$ kJ·mol$^{-1}$, and $\Delta S^{\neq} = -54\pm8$ J·K$^{-1}$· mol$^{-1}$).[6]

### Mechanism of the Electron Self-exchange Reactions

The remarkably high values of the rate constants and some unusual $\Delta H^{\neq}$ magnitude for the exchange of the σ* ($3_{dx^2-y^2}$) electron between the $Cu^{II}L_2$ and $[Cu^{III}L_2]I_n$ complexes are difficult to account for by an ordinary outer-sphere mechanism. We therefore suggest a special outer-sphere mechanism of this process, involving prior formation of a fairly stable associate of reagents (intermediate) − $Cu^{II}L_2I_nCu^{III}L_2$ − in which the essential delocalization of the electron density through the orbitals of the copper and the bridging iodine atoms is achieved, followed by an efficient electron transfer.

Direct evidence of the formation of the $Cu^{II}L_2I_3Cu^{III}L_2$ intermediate was deduced by us from comparison of the ESR spectra of the $5\cdot10^{-3}$ M $Cu^{II}L_2$ solutions in $CH_2Cl_2$ (or $CH_2Cl_2$/toluene 1:1) without and with $I_2$ ($3.8\cdot10^{-3}$ M). At this $I_2$ concentration − according to the thermodynamic data (Table 1) − as much $[Cu^{III}L_2]I_3$ complex arises as $Cu^{II}L_2$ remains (ca. $2.5\cdot10^{-3}$ M). In liquid solutions at 293 K, the obtained isotropic spin-Hamiltonian parameters for $Cu^{II}L_2$ without and with $I_2$ are the same within the limits of experimental error [$g_o = 2.048\pm0.001$ and $A_o = (75.8\pm0.5)\cdot10^{-4}$ cm$^{-1}$] and close to the literature data for $Cu^{II}L_2$ solutions in other noncoordinating solvents.[47,48] In frozen solutions at 77 K, alternatively, the anisotropic ESR spectra of $Cu^{II}L_2$ without and with $I_2$ differ from one another markedly [Figure 5 (*a*) and (*b*)]. Computer simulation of the ESR spectra in view of the known relations[49] by the program produced previously[50] enabled the following parameters of the axial-symmetry spin-Hamiltonian to be determined: $g_{\|} = 2.087$, $g_{\perp} = 2.025$, $A_{\|}^{63} = 163.4\cdot10^{-4}$ cm$^{-1}$, $A_{\|}^{65} = 174.8\cdot10^{-4}$ cm$^{-1}$, $A_{\perp} = 43.1\cdot10^{-4}$ cm$^{-1}$ for the (*a*) spectrum, as well as $g_{\|} = 2.090$, $g_{\perp} = 2.027$, $A_{\|}^{63} = 160.5\cdot10^{-4}$ cm$^{-1}$, $A_{\|}^{65} = 171.8\cdot10^{-4}$ cm$^{-1}$, $A_{\perp} = 41.0\cdot10^{-4}$ cm$^{-1}$ for the (*b*) spectrum (the *g* and *A* parameters were calculated with an accuracy of $\pm0.001$ and $\pm0.5\cdot10^{-4}$ cm$^{-1}$, respectively; in parallel orientation the hyperfine lines due to the two isotopes $^{63}Cu$ and $^{65}Cu$ are clearly resolved). The anisotropic parameters of the (*a*) spectrum agree closely with those reported for $Cu^{II}L_2$ in noncoordinating solvents.[47,48] Increases in the $g_{\|}$ and $g_{\perp}$ values and decreases in the $A_{\|}$ and $A_{\perp}$ values in going from spectrum (*a*) to spectrum (*b*) (Figure 5) are typical both for the axial adduct formation and for the self-association of copper(II) complexes.[47,48] Consequently, the spectrum (*b*) parameters are consistent with the formation of the $Cu^{II}L_2I_3Cu^{III}L_2$ intermediate with the axial bridging iodine atom or the self-associated complex,[47] which involves fairly strong axial Cu−S interactions, as with the $Cu_2L_4$ dimeric unit of the $Cu^{II}L_2$ monocrystal.[51] However the comparatively small changes in the *g* and *A* parameters with the $[Cu^{III}L_2]I_3$ present correlate better with the first of the intermediate structures.

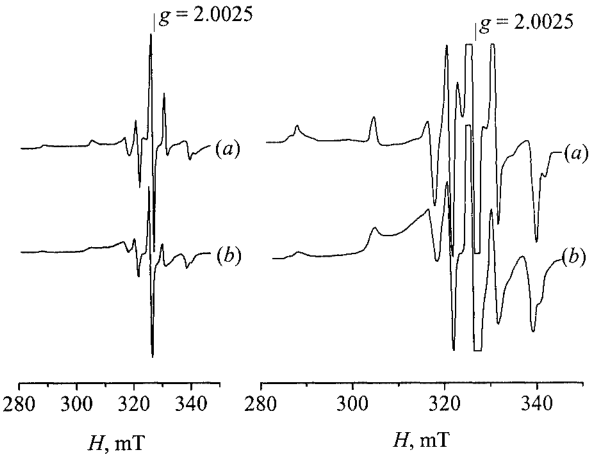

Figure 5. ESR spectra of the $5\cdot10^{-3}$ M $Cu^{II}L_2$ solutions in $CH_2Cl_2$/toluene 1:1 (*a*) and $CH_2Cl_2$ (*b*) without (*a*) and with $I_2$ (*b*) at 77 K, $c_{I_2} = 3.8\cdot10^{-3}$ M

The formation of the $Cu^{II}L_2I_3Cu^{III}L_2$ intermediate with the bridge coordination of the $I_3^-$ terminal iodine atom was confirmed by density functional theory (DFT) quantum-chemical computations (B3LYP version) with the Gaussian 98 and Jaguar program packages.[52,53] To save computation time, four ethyl groups of the ligands in the copper(II) or copper(III) complexes were in all cases replaced by methyl groups on the assumption that this should not essentially influence the geometry characteristics and electron density distribution in the immediate environment of the metal atom. The calculations were performed in three steps. Initially, optimization of the $Cu^{II}L_2$ and $[Cu^{III}L_2]^+$ geometry in vacuum was carried out by application of the Gaussian 98 program with the use of the standard 3-21G* basis set on the assumption that both complexes have $D_{2h}$ symmetry. Some computation results are given in Table 3. Note that the deduced surroundings of copper in the $Cu^{II}L_2$ and $[Cu^{III}L_2]^+$ species are close to square-planar and the calculated Cu−S bond lengths in $Cu^{II}L_2$ (2.328 Å) and $[Cu^{III}L_2]^+$ (2.194 Å) are in good agreement with those obtained by X-ray structure analysis for crystals of $Cu^{II}L_2$ (2.31 Å[51]) and $[Cu^{III}L_2]I_3$ (2.21 Å[5]). In addition, for the $I_3^-$ anion in vacuum the calculated I−I distances are 2.998 Å and the effective atomic charges are −0.060 and −0.470

Table 3. Total energies ($E_0$), averaged Cu−S bond lengths ($R$), effective atomic charges ($Q$), and atomic spin densities (ASD) computed at the B3LYP/3-21G* level for the $Cu^{II}L_2$, $[Cu^{III}L_2]^+$, $Cu^{II}L_2{*}$, and $[Cu^{III}L_2{*}]^+$ species in vacuum, as well as for $Cu^{II}L_2$, $Cu^{III}L_2I_3$, and $Cu^{II}L_2I_3Cu^{III}L_2$ intermediate in dichloromethane ($Cu^{II}L_2{*}$ is the $Cu^{II}L_2$ species with the fixed geometry optimized for the $Cu^{III}$ complex and $[Cu^{III}L_2{*}]^+$ is the $[Cu^{III}L_2]^+$ species with the geometry optimized for the $Cu^{II}$ complex)

| Species | $E_0$ [Hartree] | $R$(Cu−S) [Å] | $Q$(Cu) [a.u.] | $Q$(S) [a.u.] | ASD(Cu) [a.u.] |
|---|---|---|---|---|---|
| In vacuum | | | | | |
| $Cu^{II}L_2$ | −3561.503209 | 2.328 | 0.511 | −0.125 | 0.711 |
| $[Cu^{III}L_2]^+$ | −3561.287141 | 2.194 | 0.357 | 0.093 | 0 |
| $Cu^{II}L_2{*}$ | −3561.488716 | 2.194 | 0.360 | −0.092 | 0.631 |
| $[Cu^{III}L_2{*}]^+$ | −3561.273059 | 2.328 | 0.523 | 0.061 | 0 |
| In dichloromethane | | | | | |
| $Cu^{II}L_2$ | −3561.540925 | 2.338 | 0.544 | −0.181 | 0.743 |
| $Cu^{III}L_2I_3$ | −24233.310823 | 2.216 | 0.307 | 0.033 | 0 |
| $Cu^{II}L_2I_3Cu^{III}L_2$ | −27794.863923 | 2.320[a] | 0.497[a] | −0.180[a] | 0.719[a] |
| | | 2.214[b] | 0.303[b] | 0.034[b] | 0[b] |

[a] For the $Cu^{II}L_2$ fragment. [b] For the $Cu^{III}L_2$ fragment.

a.u. for the central and the terminal iodine atoms, respectively. These results are consistent with the data from previous $I_3^-$ computations.[17−19]

In the second step, the total energy of the $Cu^{II}L_2$ complex at the fixed geometry optimized for the $Cu^{III}$ complex {$Cu^{II}L_2{*}$} and that of the $[Cu^{III}L_2]^+$ species at the geometry optimized for the $Cu^{II}$ complex {$[Cu^{III}L_2{*}]^+$} were computed with the Gaussian 98 program for vacuum (Table 3). The difference between the $Cu^{II}L_2{*}$ and $Cu^{II}L_2$ species energies gives the inner-sphere reorganization energy[54−56] of the $Cu^{II}L_2$ complex at electron transfer, and amounts to 38.1 kJ/mol (see Table 3). Similarly, the $[Cu^{III}L_2]^+$ inner-sphere reorganization energy is defined as the difference between the $[Cu^{III}L_2{*}]^+$ and $[Cu^{III}L_2]^+$ energies (37.0 kJ/mol, Table 3). By this means the total inner-sphere reorganization energy ($\lambda_{in}$) for the electron self-exchange reaction is $\lambda_{in}$ = 38.1 + 37.0 = 75.1 kJ/mol. Because the values of the $Cu^{II}L_2$ and $[Cu^{III}L_2]^+$ inner-sphere reorganization energies are very close, the $\lambda_{in}$ magnitude can also be calculated by assuming a parabolic approximation (Marcus equation)[54,55] and starting from the experimental data.

The Marcus equation gives $\lambda_{in}$ in Equation (7)[54−56]

$$\lambda_{in} = \sum_j \frac{f_j^R f_j^P}{f_j^R + f_j^P} \cdot (\Delta q_j)^2 \tag{7}$$

where $f_j^R$ is the $j$th normal mode force constant in the reactants, $f_j^P$ is that in the products, and $\Delta q_j$ is the difference in equilibrium value of the $j$th normal coordinate in the oxidized and reduced states. We restrict our consideration only to the full-symmetric vibrations $\nu(a_1)$. For these vibrations, by using the Cu−S stretching frequencies in the dithiocarbamate complexes $Cu^{II}L'_2$ (376−404 $cm^{-1}$), $[Cu^{III}L'_2]I_3$ (400−402 $cm^{-1}$), and $[Cu^{III}L'_2]I_5$ (390−404 $cm^{-1}$),[4] we set $f_j^R \approx f_j^P \approx f$ = 300 $N\cdot m^{-1}$. On the basis of the X-ray data for $Cu^{II}L_2$ [51] and $[Cu^{III}L_2]I_3$,[5] the $\Delta q_j$ value is 0.10 Å. At the $f$ and $\Delta q_j$ values given, from Equation (7) we have: $\lambda_{in}$ = 72.4 kJ/mol. Hence, the $\lambda_{in}$ values obtained above by the DFT calculations and Equation (7) are in close agreement. In the third step of the quantum-chemical computations, the full geometry optimization of the $Cu^{II}L_2$ and $[Cu^{III}L_2]I_3$ species and the intermediate $Cu^{II}L_2I_3Cu^{III}L_2$ in dichloromethane solutions was performed by application of the Jaguar program[53] at the B3LYP/3-21G* level, with the Poisson−Boltzman SCRF model. Certain of the computed parameters are given in Table 3. We emphasize that no imaginary frequencies were found either for the initial complexes or for the optimized $Cu^{II}L_2I_3Cu^{III}L_2$ intermediate; this eliminates the possibility of the consideration of the intermediate as a transition state. From the frequency computations, the thermal correction to enthalpies required for going from 0 to 298 K were deduced. The optimized structure of the $Cu^{II}L_2I_3Cu^{III}L_2$ intermediate is rather intriguing (Figure 6). In particular, two metallo-chelates are not coplanar, with the $Cu^{II}-I_1-Cu^{III}$ angle with the bridging $I_3^-$ iodine atom ($I_1$) and the dihedral angle $C(S_2)-Cu^{III}-I_1-I_2$ being 153.5° and 87.0°, respectively. The $Cu^{III}-I_1$, $Cu^{II}-I_1$, and $Cu^{II}-Cu^{III}$ distances were found to be 2.978, 4.008, and 6.805 Å, respectively. The $Cu^{III}-I_1$ distance is very close to the length of the axial $Cu^{II}-I$ bond in the crystal of (2,6-diacetylpyridine dihydrazone)diiodocopper(II)·$1/2I_2$ (2.974 Å),[57] but markedly different from the $Cu^{III}-I$ distance in the $[Cu^{III}L_2]I_3$ monocrystal (3.48 Å),[5] in which each copper(III) atom is axially bound with two terminal iodine atoms of two $I_3^-$ groups. In the bridged $I_3^-$ anion, the $I_1-I_2$ and $I_2-I_3$ bond lengths are 3.184 and 3.094 Å, respectively, and differ slightly from those in the optimized $[Cu^{III}L_2]I_3$ complex (3.166 and 3.098 Å), but far exceed the equal I−I distances in the $I_3^-$ anion of the $[Cu^{III}L_2]I_3$ crystal (2.92 Å).[5]

The calculated values of the effective charges on the bridging ($I_1$), central ($I_2$), and terminal ($I_3$) iodine atoms of $I_3^-$ are −0.231, −0.061, and −0.385, respectively, in the intermediate, as compared to −0.292 ($I_1$), −0.071 ($I_2$), and −0.391 ($I_3$) in the initial $[Cu^{III}L_2]I_3$ complex. Hence, part of the bridged $I_3^-$ charge (−0.324) is delocalized on the $Cu^{III}L_2$ fragment (−0.265) and the $Cu^{II}L_2$ fragment (−0.059) of the $Cu^{II}L_2I_3Cu^{III}L_2$ intermediate. According to the data in Table 3, the formation energy of the intermediate in $CH_2Cl_2$ is $E_0$ = $E_0(Cu^{II}L_2I_3Cu^{III}L_2)$ − $E_0(Cu^{II}L_2)$

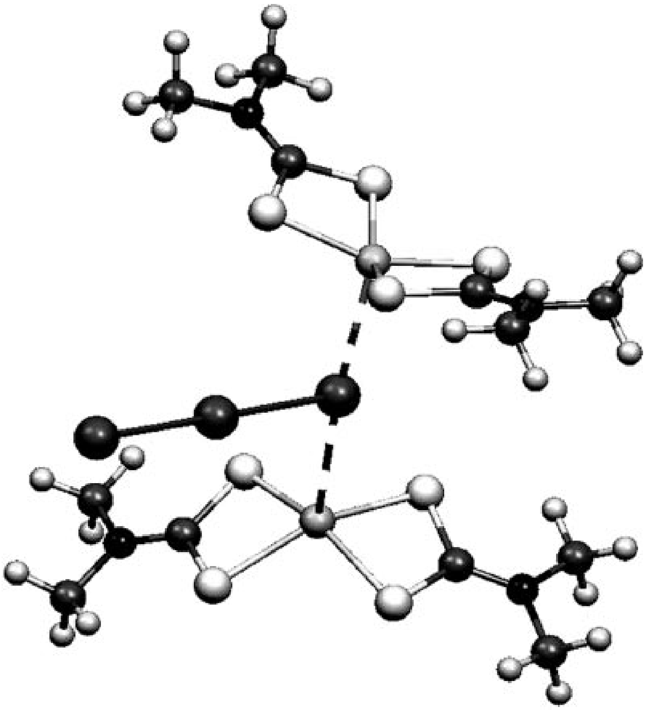

Figure 6. The structure of the $Cu^{II}L_2I_3Cu^{III}L_2$ model intermediate for the copper(II)/copper(III) electron self-exchange reaction optimized by the DFT method (the copper(III) chelate is positioned below)

$- E_0(Cu^{III}L_2I_3) = -0.012175$ a.u. $= -32.0$ kJ/mol. If the thermal correction to enthalpies ($\delta H = 1.8$ kJ/mol) is taken into account, the $Cu^{II}L_2I_3Cu^{III}L_2$ intermediate formation enthalpy can be estimated as $-30.2$ kJ/mol. From similar computations it follows that the alternative intermediate with the 1,3-bridging mode of triiodide at the designed $C_i$ symmetry has a formation enthalpy of only $-21.1$ kJ/mol and can be regarded as less probable than the above fully optimized intermediate. It should be added that the intermediate of composition $Cu^{II}L_2I_5Cu^{III}L_2$ differs from $Cu^{II}L_2I_3Cu^{III}L_2$ (Figure 6) only by the addition of $I_2$ to one of the terminal atoms of the $I_3^-$ anion.

It is appropriate to compare the value of the $Cu^{II}L_2I_3Cu^{III}L_2$ intermediate formation enthalpy discussed above with the estimation of this parameter for the dichloromethane solution following from an analysis of the activation enthalpy (Table 2) under the conditions of adiabatic electron transfer. To do this we examine the relation for the electron self-exchange rate constant $k_e$[55,56,58]

$$k_e = K_A \nu_n \kappa_{el} \Gamma_\lambda \exp(-\Delta G^*/RT) \tag{8}$$

with

$$\Delta G^* = \Delta G^*_{out} + \Delta G^*_{in} \tag{9}$$

where $K_A$ is the stability constant for the formation of an encounter complex with an appropriately oriented configuration (intermediate), $\nu_n$ is an effective nuclear vibration frequency that takes the activated reactants on to products, $\kappa_{el}$ is an electronic transmission coefficient ($\kappa_{el} \leq 1$), $\Gamma_\lambda$ is a nuclear tunneling factor ($\Gamma_\lambda \geq 1$), and $\Delta G^*$ is the free energy of activation related to the reorganization energy ($\lambda$) for electron transfer ($\lambda = 4\Delta G^*$), including contributions from both the outer-sphere reorganization energy ($\lambda_{out} = 4\Delta G^*_{out}$) and the inner-sphere reorganization energy ($\lambda_{in} = 4\Delta G^*_{in}$). Let us evaluate the $\Delta G^*_{out}$ contribution for the reaction under investigation.

From the X-ray data,[5,51] the $[Cu^{III}L_2]I_n$ and $Cu^{II}L_2$ reactants can be thought of as two identical extended ellipsoids with semi-axes $a = 7.5$ Å, $b = 2.5$ Å, and $c = 1.5$ Å (the $I_3^-$ and $I_5^-$ anions are not taken into account because they retain their charges during the course of the electron-transfer reaction and their polarizability may be regarded as approximating the $CD_2Cl_2$ polarizability). In the framework of the dielectric continuum model, Equations (10) and (11) were obtained for interaction of two conducting nonpolarizable ellipsoids contacting along the short semi-axis $c$.[59]

$$\Delta G^*_{out} = \frac{(\Delta e)^2}{4}\left(\frac{1}{D_{op}} - \frac{1}{D_s}\right)\left(\frac{F(\nu,q)}{\sqrt{a^2 - c^2}} - \frac{1}{R}\cdot g\right) \tag{10}$$

$$g = 1 + \frac{2c^2 - a^2 - b^2}{3R^2} + \frac{abc}{R^3} + \frac{4\left[8c^4 + 3\left(a^4 + b^4\right) - 8c^2\left(a^2 + b^2\right) + 2a^2c^2\right]}{15R^4} \tag{11}$$

In these equations, $\Delta e$ denotes the charge transferred from one reactant to the other, $D_s$ and $D_{op}$ are the static and optical (square of refractive index) dielectric constants of the solvent, respectively, $R$ is the center-to-center separation distance in the reacting pair during the electron transfer, and $F(\nu,q)$ is the elliptic integral of the first kind[60] with $\nu = \arcsin[(a^2 - c^2)/a^2]^{1/2}$ and $q = [(a^2 - b^2)/(a^2 - c^2)]^{1/2}$. At the ellipsoid parameters specified above, the $F(\nu,q)$ value is 2.03[60] and the $[(a^2 - c^2)]^{1/2}/F(\nu,q)$ ratio is 3.62 Å. For the intermediate in $CD_2Cl_2$ at $R = 6.8$ Å (Figure 6), $D_s = 8.93$, and $D_{op} = 2.020$[61] (298 K), it follows from Equations (10) and (11) that $\Delta G^*_{out} = 2.2$ kJ/mol. We emphasize that the low value of $\Delta G^*_{out}$ for the reaction under consideration is caused both by the moderate magnitude of the ($D_{op}^{-1} - D_s^{-1}$) parameter for dichloromethane and by the close contact of two ellipsoids with quite large volumes.

Thus, according to Equation (9) with the above value $\lambda_{in}$ (75.1 kJ/mol), we can assume that $\Delta G^* = \Delta G^*_{out} + \Delta G^*_{in} = 2.2 + 18.8 = 21.0$ kJ/mol. Knowledge of $\Delta G^*$ enables the enthalpy of the intermediate formation ($\Delta H_A$) to be calculated for the corresponding stability constant $K_A$. At $\Delta S^* \approx 0$,[55] from relations (8) and $K_A = \exp[(-\Delta H_A + T\Delta S_A)/RT]$, in conjunction with the Eyring equation, we obtain: $\Delta H^{\neq} = \Delta H_A + \Delta G^*$. Hence, with regard to the experimentally determined $\Delta H^{\neq}$ value (Table 2), it follows that $\Delta H_A = \Delta H^{\neq} - \Delta G^* = 6.1 - 21.0 = -14.9$ kJ/mol. The difference between the values of the $Cu^{II}L_2I_3Cu^{III}L_2$ intermediate formation enthalpy calculated by the semiempiric approach ($-14.9$ kJ/mol) and by the DFT method ($-30.2$ kJ/mol) can be assigned both to the approximations of the dielectric continuum model[59] and to incomplete accounting for solvation effects in the DFT computations. In any case the reasonable $\Delta H_A$ values obtained provide considerable support for the stability of the proposed and found intermediate (Figure 6).

Hence, in terms of the proposed mechanism, the remarkably high values of the electron-transfer rate constants for the system involved derive both from the particular structure of the intermediate and the favorable dielectric properties of dichloromethane. To obtain greater insight into the given mechanism we are performing further investigations of the solvent effects on the kinetics of electron self-exchange reactions between the copper(II) and copper(III) dithiocarbamates.

## Experimental Section

**Materials**. The $CH_2Cl_2$ and $CD_2Cl_2$ solvents were purified prior to use by standard method,[62] dried, and stored over 4 Å molecular sieves. Crystal iodine, $CuSO_4 \cdot 5H_2O$, $NaS_2CNEt_2 \cdot 3H_2O$ (analytical grade, Reakhim), and $Et_4NI$, after recrystallization, were used for preparation of solutions. The $Cu^{II}L_2$ and $[Cu^{III}L_2]I_3$ complexes were synthesized by literature methods.[4,5] For the $Cu^{II}L_2$, $C_{10}H_{20}CuN_2S_4$ (360.08), calcd. C 33.36, H 5.60, N 7.78, S 35.62; found C 32.98, H 5.62, N 7.79, S 35.32; for the $[Cu^{III}L_2]I_3$, $C_{10}H_{20}CuI_3N_2S_4$ (740.80), calcd. C 16.21, H 2.72, N 3.78, S 17.31; found C 16.27 H 2.50, N 3.62, S 17.70. The $[Cu^{III}L_2]I_5$ compound was isolated for the first time.

**Synthesis of Bis(*N*,*N*-diethyldithiocarbamato)copper(III) Pentaiodide, $[Cu^{III}L_2]I_5$:** A benzene solution (4 mL) of $I_2$ (20.3 mg, $1.6 \cdot 10^{-4}$ mol) was added to a dichloromethane solution (8 mL) of $Cu^{II}L_2$ (5.8 mg, $1.6 \cdot 10^{-5}$ mol). The resulting solution was allowed to stand in the refrigerator for a week. The grown crystals were collected, washed with hexane, and dried. The product constitutes lustrous brown-black crystals, m.p. 140−141 °C. For the $[Cu^{III}L_2]I_5$, $C_{10}H_{20}CuI_5N_2S_4$ (994.60), calcd. C 12.08; H 2.03; N 2.82; S 12.90; found C 12.02; H 1.92; N 2.73; S 12.94. Unfortunately it was impossible to perform Cu and I elemental analyses for technical reasons.

**Investigation Methods:** The UV/Vis absorption spectra were obtained on a LOMO Model SF 46 spectrophotometer with a thermostat in the 278−308 K temperature range, in 1.0 and 0.1 cm quartz cells. The optical densities were measured with an accuracy of ±1%. The $^1H$ NMR spectra were recorded on a Bruker WH 90 spectrometer ($\nu$ = 90 MHz) by 400−1000 acquisitions in $CD_2Cl_2$ solutions at temperatures from 248 to 298 K. Variable-temperature measurements were monitored by a Bruker temperature control unit. Signals from residual solvent protons were used as internal references. Transverse relaxation times ($T_2$) for protons of the methyl and methylene groups of the coordinated L ligands were evaluated from the NMR line-widths ($\Delta\nu_{1/2}$, Hz) by the relation[45] $T_2^{-1} = \pi\Delta\nu_{1/2}$ with an accuracy of ±5%. ESR spectra were recorded on a Model RE-1306 ESR spectrometer ($\nu$ = 9.2 GHz), at 100 KHz magnetic-field modulation.

Constants and thermodynamic parameters of equilibria in the above two systems were determined from the dependence of the molar absorption coefficient ($\varepsilon$) upon the $Et_4NI$ or $I_2$ concentrations at 5−7 values of temperature and $\lambda$ = 365 or 400 nm. All calculations of the equilibrium constants were made with the aid of the CPESSP computer program.[63] This program is based on the minimization of a $F$ function,[64] $F = \Sigma_j(X_{\mathrm{exptl},j} - X_{\mathrm{calc},j})^2 \cdot (\sigma X_{\mathrm{exptl},j})^{-2}$, where $X_{\mathrm{exptl},j}$ and $X_{\mathrm{calc},j}$ are the experimental and calculated properties, respectively, $j$ is the experiment number ($N$ experiments), and $\sigma$ is the relative error of the measurement. The reliability of the results obtained with this procedure was evaluated by the Fisher criterion by using the computed $F_{\mathrm{min}}$ value and the experimental error as described.[64]

Rate constants and activation parameters of the electron self-exchange reactions in the $Cu^{II}L_2/I_2/CD_2Cl_2$ system were calculated from the dependence of the NMR line-widths upon the $I_2$ and $Cu^{II}L_2$ concentrations at several temperatures with regard to the equilibrium constants obtained. Precipitation of a quantity of the copper(III) compounds at low temperatures was controlled by the integral intensity of the NMR signals. A poor solubility of these compounds at $T < 268$ K has given no way of estimating the NMR line widths at lower temperatures.

**Electronically Published Supporting Information:** Tables of data for the computations of the equilibrium constants with the $Et_4NI_3$, $Et_4NI_5$, $[Cu^{III}L_2]I_3$, and $[Cu^{III}L_2]I_5$ formation and the rate constants of the electron self-exchange reactions at different temperatures (4 pages, Tables S1−S4). Ordering information is given on any current masthead page (see footnote on the first page of this article).

## Acknowledgments

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