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# Hush theory in a copper mixed valence bioinorganic model generated photochemically

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## Abstract

In the present study a copper mixed valence (MV) compound has been generated photochemically from the $(CH_3–COO)_2Cu(II)–Cu(II)(OOC–CH_3)_2$ dimeric species in 95/5% (vol./vol.) methanol/acetic acid mixture as solvent. The MV species shows two intervalence (IT) bands at 19.6 and 10.4 kK and seven complex lines in the EPR spectra at room temperature. Although the two bands are IT bands in character, only the second (960 nm) could be related through the Hush and Hopfield theories to a thermal electron transfer process between the copper centers with kinetic parameters $\Delta G^{\neq}=21.6$ kJ mol$^{-1}$ and $k_{th}=1.2\times10^{9}$ s$^{-1}$ (Hush) or $4.0\times10^{11}$ s$^{-1}$ (Hopfield) at 298 K and related to the change from $(d_{x^2-y^2})^2Cu(I)–(d_{x^2-y^2})Cu(II)$ to $(d_{x^2-y^2})^1Cu(II)–(d_{x^2-y^2})^2Cu(I)$ electronic configuration ($D_{4h}$ symmetry for each copper center). The electronic assignation of the more energetic band is also discussed. The value obtained for $k_{th}$ is in the range measured by EPR spectroscopy for other Cu(II)–Cu(I) dimeric systems and provides evidence for the validity of the essence of the theoretical approach in copper binuclear systems although the value for the electronic coupling parameter is relatively high. The complex studied in this work has some characteristics in common with those of the type III copper observed in copper oxidases in its MV state such as: dimeric structure with tetragonal environment for the coppers, with oxygen perhaps as bridging ligand, EPR signal related to one unpaired electron interacting with both coppers and with $k_{th}$ values which compare well with some biological systems; so we believe it is a good bioinorganic model for type III copper in multicopper oxidases.

## Introduction

Mixed valence compounds (MV) play an important role in many fields [1]; in particular the electron transfer properties of some metalloproteins in biological processes have been related to mixed valence systems [2]. In the present study a copper mixed valence compound has been generated photochemically from the Cu(II)–Cu(II) acetate dimer in non-aqueous solution. The mixed valence dimer may be a suitable model for the electron transfer communication between metal centers in copper proteins. The compound obtained has similar optical absorption properties as the species synthesized by Sigwart *et al.* [3] starting from $Cu(I)(CH_3CN)_4ClO_4$ and $Cu(II)(ClO_4)_2$ in acetic–methanol solution.

The treatment of Hush [4], Marcus [5], Hopfield [6a] and Jortner [6b] to the intervalence transfer (IT) absorption bands of the mixed valence dimer renders information about the kinetic parameters for the electron transfer process. Additional information about species in solution and on the structure of the mixed valence dimer is also discussed.

## Experimental

$(CH_3–COO)_2Cu\cdot H_2O$ p.a. Merck was used without further purification. Glacial acetic acid (AcOH) 100% p.a. Merck and methanol (MeOH) (Merck-Uvasol spectroscopic grade) were used directly. Solutions of the cupric acetate dimer $(CH_3COO)_4Cu_2$ were prepared by dissolving $(CH_3COO)_2Cu\cdot H_2O$ in MeOH/AcOH mixtures to obtain solutions around $6\times10^{-3}$ mol dm$^{-3}$ in copper(II). The violet mixed valence compound was generated *in situ* by irradiation of the cupric acetate dimer solution with a medium pressure 400 W Hg lamp, in a stoppered cell. Since the photochemical generation of the mixed valence complex is accompanied by formation of a copper mirror on the cell window, the reaction was carried out in a four-window quartz cell, so the spectra could be taken perpendicularly to the irradiated direction. Degassing was not necessary to generate the violet mixed valence complex, which is stable in the stoppered cell at least for 5 h. When

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the cell is open, it is possible to see the oxygen diffusion into the solution by the change of the violet color to the original green of the Cu(II)–Cu(II) dimeric species. The UV–Vis and near-IR spectra were recorded in a Cary 17 spectrophotometer. The EPR spectra were recorded in a Varian 4502 spectrometer for which the violet compound was generated *in situ* by irradiation of the solution in a plain EPR cell for a few minutes to avoid interference of the copper mirror.

## Results and evaluation

The UV–Vis and near-IR spectrophotometric characterization of the $(CH_3\text{–}COO)_2Cu(II)\text{–}Cu(I)\text{-}(OOC\text{–}CH_3)_2^-$ complex (differential spectra, Fig. 1(b)), shows a band centered at 508 nm (19.6 kK) and a second broad band around 960 nm (10.4 kK), which are absent in the parent Cu(II)–Cu(II) compound (Fig. 1(a)). Although the two new bands show a different shape, when they are represented in wavenumber units ($\bar{\nu}$), both of them show the typical characteristics of the intervalence bands [4] (Fig. 2). Since $(CH_3\text{–}COO)_4Cu_2(II)$ in solution is in equilibrium with the monomeric species $(CH_3\text{–}COO)_2Cu(II)$, the concentration given in Fig. 1(a) for the $(CH_3\text{–}COO)_2Cu(II)\text{–}Cu(II)(OOC\text{–}CH_3)_2$ species was calculated from the absorption at 370 nm ($\epsilon \approx 105$ l mol$^{-1}$ cm) which has been given as characteristic of the dimeric complex, although its assignation is controversial [7, 8].

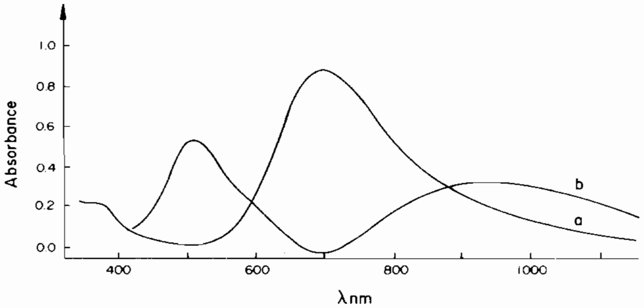

Fig. 1. UV–Vis and near-IR spectrum in 95/5% (vol./vol.) methanol/acetic acid mixture as solvent: (a) $2.3\times10^{-3}$ mol/dm$^3$ solution of $(CH_3\text{–}COO)_2Cu(II)\text{–}Cu(II)(OOC\text{–}CH_3)_2$; (b) $1.3\times10^{-3}$ mol/dm$^3$ solution of $(CH_3\text{–}COO)_2Cu(II)\text{–}Cu(I)\text{-}(OOC\text{–}CH_3)_2$ generated *in situ* by UV irradiation in a 1 cm four-window quartz stoppered cell of the non-degassed solution (a), using solution (a) as reference.

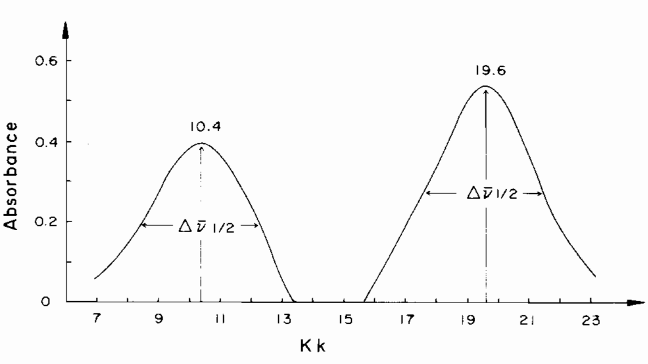

Fig. 2. Intervalence bands of the mixed valence species $(CH_3\text{–}COO)_2Cu(II)\text{–}Cu(I)(OOC\text{–}CH_3)_2$ in 95/5% (vol./vol.) methanol/acetic acid mixture as solvent, obtained from Fig. 1(b).

The concentration for the $[(CH_3\text{–}COO)_2Cu(II)\text{–}Cu(I)(OOC\text{–}CH_3)_2]$ species was calculated from the extinction coefficient given by Sigwart *et al.* [3] for the 508 nm band; from the concentration value obtained we were able to calculate the extinction coefficient for the near-IR band (Table 1). Considering that the $\alpha$ value for the 508 nm band places the MV compound in the Robin and Day class II [9] and the spectra shown in Fig. 1 of Sigwart *et al.* [3] do not show any difference for the d–d ligand field transition between the Cu(II)–Cu(II) and Cu(II)–Cu(I) species, the differential spectra of the MV complex (Fig. 1(b)) was obtained using solutions (a) as reference. The spectra of solution (b) oxidized by oxygen is the same as (a) but with slightly smaller absorbance values due to the Cu$^0$ formed on irradiation. Since the 508 and 960 nm bands appear only in the MV compound (Fig. 1(b)) with the typical characteristics of intervalence bands (Fig. 2), they may be tentatively assigned to transitions such as

$$[(CH_3\text{–}COO)_2Cu(II)\text{–}Cu(I)(OOC\text{–}CH_3)_2]^- \xrightarrow{E_{op}=h\nu} [(CH_3\text{–}COO)_2Cu(I)\text{–}Cu(II)(OOC\text{–}CH_3)_2]^- \tag{1}$$

which are considered intervalence transitions (IT).

The EPR spectra of the photochemically generated species (Fig. 3) show more than four copper parallel hyperfine lines (which might be identified as seven complex lines) indicating the unpaired electron is interacting with both copper centers.

Table 1 contains the experimental and calculated values of $\Delta\nu_{1/2}$ (bandwidth at half-height) from eqn. (2), for the homonuclear case, i.e. $\Delta E = 0$ [4].

$$\Delta\nu_{1/2} = (2.31\times10^3\nu_{max})^{1/2} \text{ with } \nu_{max} \text{ in cm}^{-1} \tag{2}$$

Considering that electronic coupling between the copper centers is weak, the extent of delocalization ($\alpha$) of the excess electron from Cu(I) into Cu(II) may be calculated for the ground state by eqn. (3) (Table 1)

$$\alpha^2 = 4.2\times10^{-4}\epsilon_{max}\,\bar{\nu}_{1/2}/(\bar{\nu}_{max}d^2) \tag{3}$$

where $\bar{\nu}_{max}$ and $\bar{\nu}_{1/2}$ are given in cm$^{-1}$ and $d$ (copper–copper distance) in Å. Since the $d$ value for the MV species is unknown we have used an average value obtained from $d$ in $(CH_3\text{–}COO)_2Cu(II)\text{–}Cu(II)\text{-}(OOC\text{–}CH_3)_2$ and $(CH_3\text{–}COO)_2Cu(I)\text{–}Cu(I)(OOC\text{–}CH_3)_2$ species, both of them determined by X-ray spectroscopy [10, 11].

TABLE 1. Intervalence absorption spectral data, electronic interaction and intramolecular electron-transfer parameters for $(CH_3COO)_2Cu(II)$–$Cu(I)(OOC$–$CH_3)_2$ generated photochemically[a]

| $\bar{\nu}_m$ (kK) | $\Delta\bar{\nu}_{1/2}$ (obs.) (kK) | $\Delta\bar{\nu}_{1/2}$ (calc.) (kK) | $\alpha$ | $V_{ab}$ (kJ mol$^{-1}$) | $\Delta G^{\#}$[c] (kJ mol$^{-1}$) | $k_{th}$ (s$^{-1}$)[d] | $k^c_{th}$ (s$^{-1}$)[e] |
|---|---|---|---|---|---|---|---|
| 19.6<br>(416)[b] | 4.0 | 6.7 | 0.072 | 16.9 | 41.9 | $2.8\times10^5$ | $9.7\times10^7$ |
| 10.4<br>(270) | 4.0 | 4.9 | 0.08 | 10.0 | 21.2 | $1.2\times10^9$ | $4.0\times10^{11}$ |

[a] 95/5% (vol./vol.) methanol–acetic acid mixture was used as solvent. [b] Extinction coefficients in l mol$^{-1}$ cm$^{-1}$ are given in parentheses. [c] $\Delta G^{\#} \simeq E_{op}/_4 - V_{ab}$ (see text) and $E_{op} = hc\,\bar{\nu}_m$. [d] Calculated from activated complex theory expression (eqn. (5)) in text. $T = 298$ K. [e] Calculated from Hopfield [6a] (eqn. (6)) in text. $T = 298$ K.

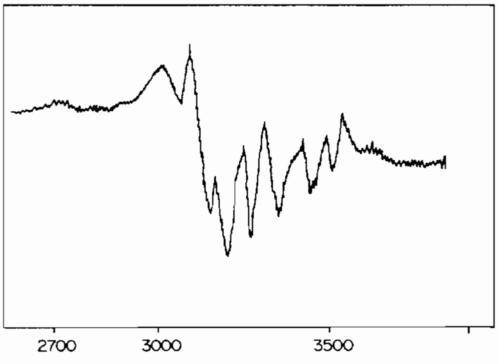

Fig. 3. EPR spectra at room temperature of the mixed valence species $(CH_3$–$COO)_2Cu(II)$–$Cu(I)(OOC$–$CH_3)_2$ generated *in situ* by UV irradiation of a non-degassed solution of the Cu(II)–Cu(II) species in a plain EPR cell.

The data for the thermal electron transfer activation energy $E^*_{th}$, and the thermal electron transfer rate constant, $k_{th}$, shown in Table 1 were calculated from the expression given by the Hush theory (eqn. (4), homonuclear case) including the effect of the resonance

$$E^*_{th} \approx \frac{E_{op}}{4} - V_{ab} \qquad (4)$$

energy [4] and the activated complex theory (eqn. (5))

$$k_{th} = \frac{k_B T}{h} \exp(-\Delta G^*/RT),$$
$$k_{th} = \frac{k_B T}{h} \exp(-E_{op})/4RT + V_{ab} \qquad (5)$$

respectively, since $T\Delta S^* \approx 0$. $V_{ab}$ is the electron exchange matrix element or resonance energy, which may be calculated as $V_{ab} < \alpha\bar{\nu}_{max}$ and related to the electronic coupling (Table 1).

From the quantum mechanical treatments of Hopfield [6a] and Jortner [6b] it was also possible to calculate rate constants for intramolecular electron transfer using the properties of IT bands (eqn. (5)) from the expression

$$k^c_{th} = \frac{2\pi^{3/2}}{h} V^2_{ab}(1/k_B T E_{op})^{1/2} \exp(-E_{op}/4RT + V_{ab}) \qquad (6)$$

*Calculation of overlap integrals*

The calculations were made using FORTICON 8. FOR program with 3d electron normalized Slater type functions in the 'double-zeta' form, i.e.

$$R_{3d} = C_1 x_{3d}(\zeta_1) + C_2 x_{3d}(\zeta_2)$$

where $x_{3d}(\zeta_1) = [(2\zeta_1)^{(2\cdot3+1)}/(2\cdot3)]^{1/2} r^{(3-1)} \exp(-\zeta_1 r)$

and the free parameters determined by Richardson *et al.* [12] maximizing the overlaps with Watsons's SCF atomic orbitals functions. The values used were:

| Cu(II) | | Cu(I) | |
|---|---|---|---|
| $\zeta_1 = 5.95$ | $C_1 = 0.6064$ | $\zeta_1 = 5.95$ | $C_1 = 0.5948$ |
| $\zeta_2 = 2.50$ | $C_2 = 0.5371$ | $\zeta_2 = 2.30$ | $C_2 = 0.5729$ |

The Cu(II)–Cu(I) distances were the same as for the $\alpha$ calculation (eqn. (3)).

## Discussion

The mixed valence compound was generated as an intermediary species in the photochemical reaction of $(CH_3$–$COO)_4Cu_2$ in MeOH/AcOH mixture as solvent, when it was irradiated in the LMCT band zone, i.e. UV zone, the following process may be assumed*

$$Cu_2(CH_3\text{–}COO)_4 \xrightarrow[\text{LMCT}]{h\nu}$$
$$[(CH_3\text{–}COO)_2Cu(II)\text{–}Cu(I)(OOC\text{–}CH_3)_2]^- \longrightarrow$$
$$Cu^0 + CH_4 + \text{other products}$$

Although we were able to generate the mixed valence species in MeOH/AcOH solvent mixed in different proportions, it was not possible to get values for $x_0$

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*$CH_4$, $CH_2O$, $C_2H_6$, $CO_2$ and $Cu^0$ where experimentally detected; unpublished results.

(molecular vibrations) and $x_1$ (solvent vibrations) contributions to the optical energy of the IT transition [5, 13] since the $E_{op}$ values showed a smooth negative slope for the dependence of $E_{op}$ versus $(1/D_{op}-1/D_s)$ suggesting the probable presence of specific interaction with some of the two solvents in the mixture.

The results given above were with a 95/5% (vol./vol.) MeOH/AcOH solvent mixture since in these conditions the concentration of the MV is the highest which allows an adequate determination of the maximum in the broad IT bands. The presence of MeOH (at least in a small%) as solvent seems to be essential for the MV photochemical generation, which is not surprising if we take into account:

(i) the possibility that MeOH like water would be preferentially coordinated in the axial position by the copper acetate dimer as opposed to acetic acid [10, 14];

(ii) coordinated MeOH as solvent seems to play an important role in the photoreduction of copper complexes [15, 16];

(iii) the more favorable oxidation–reduction potential of the Cu(II)/Cu(I) couple in MeOH [17, 18].

From the results given in Table 1 for $\Delta\nu_{1/2}$ and $\alpha$ it appears that the behavior of the near-IR IT band for the MV compound is that expected for the optical electron transfer transition of class II in the Robin and Day classification [9].

Before the analysis of the results for the high energy IT band, the assignation of both bands must be considered; although more than one intervalence transfer band may occur, the IT band energy is simply related to a barrier for the thermal electron transfer process (eqns. (4) and (5)) only when the electronic state of the metal ions is the same in reactant Cu(II)–Cu(I) and product Cu(I)–Cu(II) (i.e. the excited state produced by light absorption is vibrational and not an electronic state) [19].

Using an orbital level scheme similar to that given for the Cu(II)–Cu(II) dimer by Hansen and Ballhausen [7] (Fig. 4), the IT bands in the Cu(II)–Cu(I) species may be assigned as follows:

(i) the absorption in the near-IR to a transition from the state associated to the $b_1^2$ Cu(I)–$b_1^1$ Cu(II) configuration to the state associated to the $b_1^1$ Cu(II)–$b_1^2$ Cu(I) configuration indicated with an arrow in Fig. 4;

(ii) the absorption in the visible may be ascribed to:

(1) from $a_1^2b_1^2$ Cu(I)–$b_1^1$ Cu(II) to
$\longrightarrow a_1^1b_1^2$ Cu(II)–$b_1^2$ Cu(I) or
(2) from $b_2^2b_1^2$ Cu(I)–$b_1^1$Cu(II) to
$\longrightarrow b_2^1b_1^2$ Cu(II)–$b_1^2$ Cu(I) or
(3) from $e^4b_1^2$ Cu(I)–$b_1^1$ Cu(II) to
$\longrightarrow e^3b_1^2$ Cu(II)–$b_1^2$Cu(I)

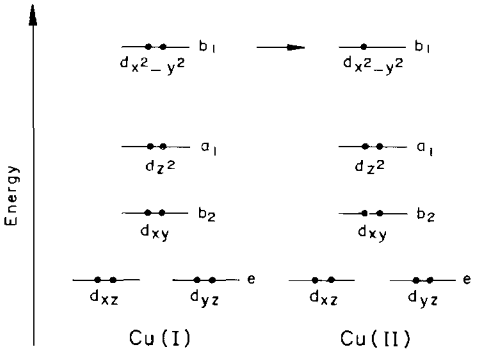

Fig. 4. Schematic representations of orbital levels for the mixed valence dimer. The relative energy level differences between Cu(I) and Cu(II) chromophores are not shown and the scheme is not drawn to scale.

Although the symmetry of the Cu(I) site in the MV species is not known [20], it may be expected to be not so different from the symmetry of the Cu(II) site, since X-ray structure studies indicate that Cu(I) acetate has a planar structure [11] (not tetrahedral as is the tendency of Cu(I) complexes). A comparison of the solid state X-ray data suggests only a small axial distortion expected for the Cu(I) site as compared to Cu(II), which does not imply a change in coordination number. Therefore it seems reasonable to use the orbital level scheme proposed by Hush and Ballhausen for the Cu(II)–Cu(II) dimer as a first approach for the Cu(II)–Cu(I) species.

Returning to the assignation analysis, the last three possible transitions suggested above involve the formation of an electronic excited state, which will require higher energy than a simple barrier for a thermal electron transfer, hence one of them may be associated with the visible IT absorption.

Following the Hush analysis [4], together with the low energy IT ($\nu_{IT}$) involving the transfer of an electron from an occupied orbital on one nucleus to an equivalent vacant orbital on the second nucleus (homonuclear system), that is, $d_{x^2-y^2}$ Cu(I) to $d_{x^2-y^2}$ Cu(II) in our system (see above, the assignation for the near-IR IT band and Fig. 4), a second intervalence transfer transition involving an excited state configuration must be expected to occur at an approximate frequency $(\nu_{IT}+\nu_{Cu(II)})$ if the interaction between the metal centers is weak; $\nu_{Cu(II)}$ is the frequency of the internal transition of the acceptor ion (d–d transition) which is around 14 kK so the second IT band must be predicted at around 24.4 kK; although the experimental band is at 19.6 kK, the results are satisfactory since the interaction between the coppers is not so weak. So, on this basis, option (3), might describe adequately the absorption in the visible range.

In the light of the electronic interpretation of the IT bands, it is now possible to understand the 'apparent' discrepancy between $\Delta\nu_{1/2}$ experimental and $\Delta\nu_{1/2}$ calculated for the $19.7\times10^3$ cm$^{-1}$ band and the fact that the associated $k_{th}$ result is more 'rapid' than would be expected since it does not have a simple relation to a thermal electron transfer barrier. The type of potential energy associated to our system for this high energy transfer is schematically shown in Fig. 5 with $\Delta E$ equal to the energy difference between $d^2{}_{z^2}(d_{x^2-y^2})^2$Cu(I)–$d^2{}_{z^2}(d_{x^2-y^2})^1$Cu(II) and $e^4d^1{}_{z^2}(d_{x^2-y^2})^2$Cu(II)–$e^3d^2{}_{z^2}$-$(d_{x^2-y^2})^2$Cu(I) state configurations. So the second absorption IT band may be formally treated as an IT band in a 'heteronuclear' system where the 'hetero' character is derived from the non-equivalence of the initial and final states involved in the transition. In this case

$$\Delta E = h\nu_{IT} - (16 \ln 2kT)^{-1} (\Delta\nu_{1/2})^2 \tag{7}$$

so the theoretical $\Delta\nu_{1/2}$ must be calculated from this expression. Although $\Delta E$ is not known, but considering that the visible IT band in our system is a 'good' Hush second class band (Fig. 2), eqn. (7) may be used to work out $\Delta E$ from the experiment $\Delta\nu_{1/2}$ value and $T = 295$ K. $\Delta E$ is evaluated as $12.6\times10^3$ cm$^{-1}$ and $E^*{}_{th}$ from eqn. (8)

$$E^*{}_{th} = \frac{E^2{}_{op}}{4(E_{op} - \Delta E)} \tag{8}$$

is 39.6 kcal, thus $k_{th} \approx 10^{-15}$ s$^{-1}$, which is a more realistic value and shows that this electron transfer has a very low probability of taking place thermally.

Otherwise the value 12.6 kK obtained for $\Delta E$ is in the order of the d–d internal band for Cu(II) ($\approx 14$ kK). Since eqn. (7) from which $\Delta E$ was calculated is independent of any transition assignation of the bands, the result is relevant and interesting. In effect this value agrees with those expected according to the interpretation of the spectra made above using the Hush theory, giving support to the assignation of the high energy IT band.

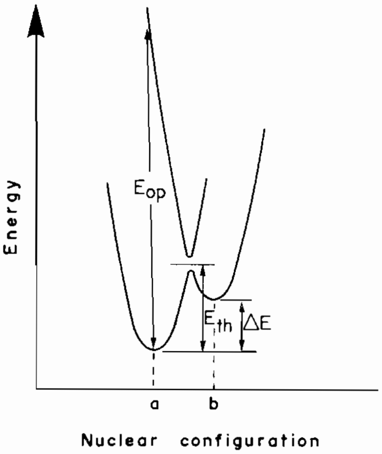

Fig. 5. Potential energy plot as a function of nuclear configuration for a weak-interaction electron transfer showing the intervalence band maximum energy ($E_{op}$), thermal activation energy ($E^*{}_{th}$) and the energy difference between $d^2{}_{z^2}(d_{x^2-y^2})^2$Cu(I)–$(d_{x^2-y^2})^1$Cu(II) and $d^1{}_{z^2}(d_{x^2-y^2})^2$Cu(I)–$(d_{x^2-y^2})^2$Cu(II) configurations.

On the other hand the $S$ ($d_{x^2-y^2}$–$d_{x^2-y^2}$) value for the Cu(II)–Cu(I) species ($1.3\times10^{-2}$) is greater than for the Cu(II)–Cu(II) dimer ($9.1\times10^{-3}$), however the results of Salomon and co-workers [21] indicate that superexchange is the fundamental mechanism for the electron transfer.

Although we were able to calculate a $k_{th}$ value with the Hush theory using spectroscopic data, it is important to find out whether or not the value is correct even within the order of magnitude. Experimental kinetics methods for measuring rates for reactions such as eqn. (1) have remained elusive, so our results have to be compared with those given for other copper binuclear complexes in which the thermal intramolecular electron transfer specific constants were measured by EPR spectroscopy. The values given are in the $10^7$–$10^{10}$ s$^{-1}$ range [22]. The result given by Sigwart *et al.* as $10^8$ s$^{-1}$ [3], as the minimum electronic exchange rate for a complex similar to the compound of this work, is of particular interest. The compared results agree in the order of magnitude and provide evidence for the validity of the essence of the theoretical approach in copper binuclear complexes, although the value of the electronic coupling parameter ($V_{ab}$) is relatively high [13]. A comparison with electron transfer processes in biological systems is rather difficult; although half-met mixed valence states for binuclear copper sites in some proteins have been generated [23], no experimental values for its interelectronic exchange have been reported [24]. Salomon and co-workers [25] have reported some IT parameters and a mixed valence analysis for half-met-L-hemocyanins. Our results compare well with some of the values given as well with the $k_{th}$s calculated from the $E_{IT}$ and $H_{AB}$ results of Salomon for $L = I^-$ in which Cu(I) shows the most distorted character towards a more tetragonal geometry. Therefore the complex studied here has some characteristics in common with the type III copper observed in copper oxidases in the MV state (and other proteins with binuclear copper active sites), for which:

(i) energy of the d–d bands requires that the coppers be in a tetragonal rather than a tetrahedral environment [26],

(ii) with oxygen perhaps as a bridging ligand [26, 27]

(iii) the EPR signal in the MV states is related to one unpaired electron interacting with both coppers [22, 23],

(iv) with IT parameters which compare well with some experimental results for half-met species in some copper proteins [25].

Finally, it may be useful to make some comments in relation to the structure of the MV complex in solution studied here. Although Cu(II) is kinetically labile, the species Cu(II)–Cu(II) in methanol/acetic acid mixture 95/5% (vol./vol.) must be the same as that in anhydrous acetic acid except perhaps that the solvent is coordinated at the axial position. Effectively, the synthesis of methanol adducts of copper acetate is made by dissolving polycrystalline copper(II) acetate dehydrated in absolute methanol; the molecular structure is dimeric and similar to the monohydrate but with a shorter copper–copper distance and, a Cu–axial ligand bond slightly longer than in the monohydrate [10]. As it was pointed out before there is no reason to believe that the presence of Cu(I) in the mixed valence species must change the structure. So it is possible that the Sigwart species [3] has the same structure as the complex evidenced in this work since the solvent conditions are similar in both works.

## Acknowledgements

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