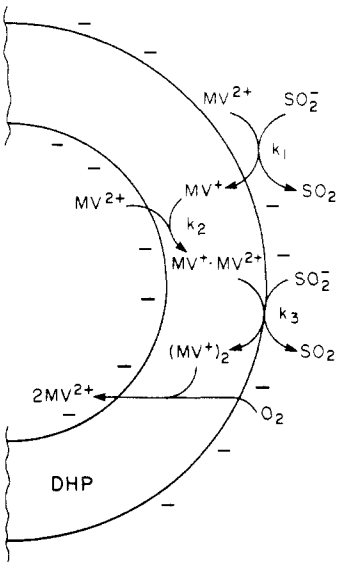

Figure 2. Reaction pathway for transmembrane redox. The k_2 step, represented as viologen dimerization, is complex.

inside–outside MV^{2+} product distribution after redox cycling was very nearly identical with the initial distribution before reduction. This result is expected since transmembrane oxidation of internal MV^+ would be electrogenic in the opposite sense to internal MV^{2+} reduction in the absence of transverse ion migration. Thus, the same forces driving inward diffusion of MV^+ during reduction drive its outward diffusion when a membrane-impermeable oxidant is used.

Reduction of MV^{2+} bound only at the external interface of DHP vesicles gave predominantly monomeric radical ion product[16] (Figure 1, solid line). The amount of monomer remained greater than 85% of the total reduced viologen at $[MV^{2+}]/[DHP]$ ratios ranging from 0.0025–0.015 and was still 40% at the very high ratio of 0.15. In contrast, when equimolar MV^{2+} was present at the opposing vesicle interfaces or when internal MV^{2+} was in excess (r = 0.01–0.04), the product optical spectrum corresponded primarily to the multimeric form of the radical[16] (Figure 1, dotted line). When external MV^{2+} was in excess, the amount of multimer formed was approximately equal to the initial concentration of MV^{2+} on the inner surface, the remainder being monomeric MV^+ radical cation (e.g., Figure 1, dot-dashed line). These observations indicate that the multimeric form of the radical is formed in a stoichiometric ratio of one viologen each from the inner and outer vesicle interfaces and that reduction of inner bound MV^{2+} is associated with aggregation.[17]

Reduction of DHP vesicles containing internally and externally bound MV^{2+} exhibited biphasic kinetics. Relative amplitudes for the two steps measured at various wavelengths indicated that monomeric and multimeric MV^+ were the principal products of the fast and slow reaction steps, respectively. These observations establish that aggregation is coincident with transmembrane redox under steady-state conditions. With $S_2O_4^{2-}$ in excess, the fast step was first order and gave a rate constant, k_1, similar to the constant for dithionite reduction of MV^{2+} in solution.[18] The rate for the slow step was about 10^2-fold less than the fast reaction step and with equimolar MV^{2+} initially at both interfaces followed simple second-order kinetics with $k_2 = 1.3\ (\pm 0.4) \times 10^4\ M^{-1}\ s^{-1}$ in 20 mM Tris, pH 8.0, 23 °C, [DHP] = 1–2 mM, and $[MV^{2+}]/[DHP]$ = 0.025–0.081; k_2 was independent of the monitoring wavelength and $S_2O_4^{2-}$ concentrations measured over the range $[S_2O_4^{2-}]$ = 0.41–2.2 mM.

A reaction scheme consistent with these facts is illustrated in Figure 2. Here, rapid reduction of externally bound MV^{2+} (k_1) precedes reduction of internally localized MV^{2+} (k_2), which occurs either by rate-limiting formation of a mixed-valent MV^{2+}–MV^+ dimer or slow electron exchange between external MV^+ and internal MV^{2+}, followed by rapid dimerization. The MV^{2+}–MV^+ dimer is subsequently rapidly reduced (k_3) to $(MV^+)_2$ by externally localized $S_2O_4^{2-}$. Upon oxygenation, the MV^{2+} ions derived from the dimer are found inside the vesicle, as expected from the system electrostatics. Since k_1, $k_3 \gg k_2$, the rate law is given by $d[MV^+]_T/dt = k_1[MV^{2+}]_o[SO_2^-] + k_2[MV^+]_o[MV^{2+}]_i$, where subscripts T, o, and i refer to total MV^+ in the system and MV^{2+} bound at outer and inner vesicle interfaces, respectively. With equimolar inner and outer $[MV^{2+}]$, $[MV^+]_o \simeq [MV^{2+}]_i$ for the slow step, so that $d[MV^+]_T/dt \simeq k_1[MV^{2+}]_o[SO_2^-] + k_2[MV^{2+}]_i^2$.

Our present efforts are directed at probing mechanistic details of the transmembrane redox step and exploring the generality of the mechanism. Consistent with our observations, a report has recently appeared[9] suggesting comparable dynamic behavior for *N,N'*-dihexadecyl-4,4'-bipyridinium^{2+}-mediated transmembrane electron transfer between $S_2O_4^{2-}$ and $Fe(CN)_6^{3-}$ ions separated by phosphatidylcholine liposomal membranes.

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Registry No. DHP, 2197-63-9; MV^{2+}, 4685-14-7; S_2, 14844-07-6.

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(17) Although the basis for preferential dimerization of MV^+ within the vesicle is presently unknown, it is not ascribable simply to a concentrating effect. The internal surface area of the DHP vesicles is about 1/3 the total area;[14] because the viologen is extensively membrane-associated, the inner localized MV^+ would be only twice the surface concentration of outer localized MV^+ when the inside/outside ratio is equimolar.

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Moderately Strong Intramolecular Magnetic Exchange Interaction between the Copper(II) Ions Separated by 11.25 Å in $[L_2Cu_2(OH_2)_2(\mu\text{-terephthalato})](ClO_4)_2$ (L = 1,4,7-Trimethyl-1,4,7-triazacyclononane)

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Owing to its fundamental importance, the study of long-range magnetic interactions has been an active field of research in recent years.[2] The terephthalato dianion has been proved to be an appropriate bridging unit to design magnetic systems with a separation of 11–12 Å between the two magnetic centers.[3-5] In all of these studies the intramolecular magnetic interactions, to the disappointment of the research workers, were negligibly small.

(1) (a) Ruhr-Universität. (b) Technische Hochschule Darmstadt. (c) Universität Heidelberg.

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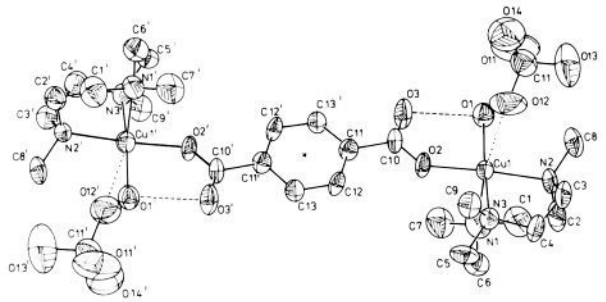

Figure 1. Structure of $[L_2Cu_2(OH_2)_2(\mu\text{-terephthalato})]^{2+}$, showing 40% probability ellipsoids. Representative distances (Å) are as follows: Cu1–N1, 2.217 (5); Cu1–N2, 2.034 (5); Cu1–O1, 2.009 (4); Cu1–O2, 1.972 (4); Cu1–O12, 2.992 (6); Cu1–Cu1′, 11.252 (4); O3–O1, 2.516 (4).

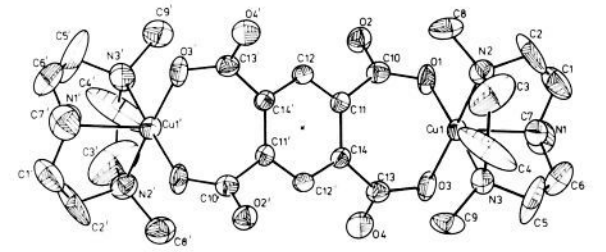

Figure 2. Structure of $[L_2Cu_2(\mu\text{-tetracarboxylatobenzene})]$, showing 40% probability ellipsoids. Representative distances (Å) are as follows: Cu1–N1, 2.188 (4), Cu1–N2, 2.035 (4); Cu1–O1, 1.942 (3); Cu1–O3, 1.949 (3); Cu1–Cu1′, 7.811 (4).

We report here a long distance (11.3 Å) moderately strong antiferromagnetic coupling ($J = -70$ cm^{-1}) between Cu(II) atoms in a μ-terephthalato complex. A second complex containing a μ-tetracarboxylatobenzene bridging unit exhibits very weak exchange interactions although the Cu···Cu separation is smaller (7.8 Å) than that in the mentioned μ-terephthalato complex. The X-ray structures of $[LCu(OH_2)(\mu\text{-terephthalato})(OH_2)CuL](ClO_4)_2$ (**1**) and $[LCu(\mu\text{-tetracarboxylato})CuL]\cdot 4H_2O$ (**2**) (L = 1,4,7-trimethyl-1,4,7-triazacyclononane)[6] are presented in Figures 1 and 2.

A crystallographic inversion center in **1** is located at the center of the benzene ring of the terephthalato ligand. The geometry around the two copper(II) ions is square-based pyramidal with two nitrogens N2 and N3 of the cyclic amine, one oxygen atom O2 of the carboxylic group, and the oxygen atom O1 of a water molecule in the basal plane and the nitrogen N1 of the amine in the apical position. The Cu(II) ion is displaced by 0.122 (2) Å from the mean basal plane toward the apex. Two perchlorate ions are in the vicinity of the Cu(II) centers (Cu1–O12 = 2.992 (2) Å). The two mean basal planes containing the CuN_2O_2 units are strictly coplanar with the terephthalato ligand with its eight carbon atoms. A strong hydrogen bond[11] (O3–O1 = 2.516 Å) may be envisaged between O1 of the coordinated water molecule and the noncoordinated oxygen atom O3 of the terephthalato anion, yielding a six-membered ring and enforcing the coplanarity of the planes of the terephthalato dianion with the mean basal plane containing the CuN_2O_2 units. The Cu···Cu distance inside a dinuclear unit is 11.252 (4) Å. The closest *inter*molecular Cu···Cu distance is 7.587 (1) Å.

Table I. Magnetic and ESR Data for **1** and **2**

compd	J/cm^{-1}	$\langle g\rangle_{mag}$	$g_\parallel$	$g_\perp$
1	−70.0	2.20	2.30	2.10
2	−0.7	2.07	2.08	2.03

The dinuclear units in **2** are also centrosymmetric. The copper environments are very similar to that of **1**, i.e., square-based pyramidal. Each carboxylic group is bound to Cu(II) in a monodentate fashion through only one oxygen atom, yielding two seven-membered rings. The two basal planes containing the O1, O3, N2, and N3 atoms are parallel to each other but make the angles 116° and 64° with the Cu–Cu vector. A Cu···Cu separation of 7.811 (4) Å inside a dinuclear unit has been found.

Variable temperature (4.2–289.5 K) magnetic susceptibility[6] data of dried powdered samples of **1** and **2** were fitted by means of least squares to the expression[7] for χ_M versus T derived from the isotropic spin Hamiltonian, $\hat{H} = -2J\hat{S}_1\cdot\hat{S}_1$, with $S_1 = S_2 = 1/2$. The results of susceptibility-fitting are listed in Table I. The X-band powder EPR spectra at 110 K of **1** and **2** are of axial type yielding two g values (Table I).[8]

The close-to-square-pyramidal geometry of the copper(II) ions in both compounds, **1** and **2**, suggests that they have $(d_{x^2-y^2})^1$ ground states, as is also evident from the ESR spectra. The major σ-pathway[10] in **1** for the interaction of these magnetic orbitals containing the unpaired electron involves the terephthalato ligand, which is copolanar with the $d_{x^2-y^2}$ orbital. Substantial antiferromagnetic coupling ($J = -70$ cm^{-1}) is therefore observed in **1**, in spite of the Cu···Cu intramolecular separation of 11.252 (4) Å. On the other hand, the noncoplanarity of the bridging ligand 1,2,4,5-tetracarboxylatobenzene with the plane of the magnetic orbitals of Cu(II), $(d_{x^2-y^2})$,[1] leads to the weak magnetic interaction ($J = -0.7$ cm^{-1}) in **2**.

In summary, this work has shown that 11.25 Å is definitely not the limit for the intramolecular magnetic interaction between two Cu(II) ions, provided the Cu(II) atoms and the bridging ligand have the proper geometry.[12] A relatively strong magnetic interaction propagated through the bridging ligand along such a distance (11.25 Å) between two copper ions has been observed.

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Supplementary Material Available: A drawing of the unit cell of **1**, tables of positional and thermal parameters and bond distances and angles for **1** and for **2**, and two figures showing the fitted susceptibility curves (14 pages). Ordering information is given on any current masthead page.

(6) (a) Piperidinium terephthalate (0.5 mmol) was reacted with $Cu(ClO_4)_2\cdot 6H_2O$ (1 mmol) and 1,4,7-trimethyl-1,4,7-triazacyclononane(L)[13] (1.5 mmol) in methanol (50 mL) and upon concentration yielded turquoise blue crystals of compound **1**. Compound **2** was prepared similarly by reacting an aqueous solution (pH 9) of 1,2,4,5-tetracarboxylatobenzene (0.5 mmol) with a methanolic solution of $Cu(AC)_2\cdot H_2O$ (1 mmol) (40 mL) and L (1.5 mmol). (b) Analytical, magnetic, and spectroscopic data. Anal. Calcd for $Cu_2C_{26}H_{46}N_6Cl_2O_{14}$ (**1**): C, 36.12; H, 5.36; N, 9.72; Cu, 14.70; ClO_4, 23.02. Found: C, 36.0; H, 5.60; N, 9.62; Cu, 14.86; ClO_4, 23.20. Anal. Calcd for $Cu_2C_{28}H_{52}N_6O_{12}$ (**2**): C, 42.47; H, 6.62; N, 10.61; Cu, 16.05. Found: C, 42.31; H, 6.81; N, 10.30; Cu, 15.91. IR (KBr cm^{-1}) 3560, 3480 (OH), 1570 and 1360 (COO), 1090, 610 (ClO_4) for **1**, 3400 (br, OH), 1590 and 1370 (COO) for **2**. Magnetic measurements were repeated three times. For magnetic measurements crystals of **2** were powdered and dried under vacuum at 60 °C over P_2O_5 for 90 h. Magnetic susceptibility [(T, K) μ_B/Cu atom]: (4.2) 0.290, (25.8) 0.389, (55.9) 0.708, (103.4) 1.243, (149.2) 1.498, and (289.5) 1.792 for **1** and (4.2) 1.548, (25.8) 1.680, (55.9) 1.737, (149.2) 1.736, and (289.5) 1.796 for **2**. (c) **1** is monoclinic, space group $P2_1/c$ (C^5_{2h}, no. 14) with a = 8.619 (4) Å, b = 14.059 (3) Å, c = 15.156 (9) Å, β = 96.25 (4)°, Z = 4, R = 4.8% for 1836 unique reflections ($I \geq 2.5\sigma(I)$). **2** is orthorhombic, space group $Pbca$ (D^{15}_{2h}, no. 61) with a = 14.400 (4) Å, b = 16.963 (5) Å, c = 16.879 (7) Å, Z = 4 and R = 5.4% for 3558 observed ($I \geq 2.5\sigma(I)$) reflections.

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(8) The zero-field splitting (D)[9] could be calculated to be 1.8×10^{-3} cm^{-1} for **1** and 4.9×10^{-3} cm^{-1} for 2 by assuming that it arises from the dipolar interaction between the two local doublets separated by 11.25 and 7.81 Å, respectively.

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(10) (a) The crystal packing diagram (Supplementary Material), devoid of any preferential packing direction, clearly rules out the possibility of *inter*molecular magnetic interactions. (b) The PF_6-salt of the cation in complex **1** also exhibits an antiferromagnetic interaction with an S–T gap of 50 cm^{-1}.

(11) The compound $[Cu_2(bipy)_2(OH_2)(\mu\text{-terephthalato})]^{2+}$ of ref 4b also exhibits a moderately strong antiferromagnetic interaction ($J = -25.9$ cm^{-1}). Lacking crystal structure determination, this interaction has been interpreted as *inter*molecular in nature. It seems very likely that this compound also contains this type of hydrogen bonds and the magnetic interaction is *intra*molecular in nature.

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