Exchange Elasticity in Copper(II) Dinuclear Cryptates

Sir:

Significant progress in the understanding of the exchange interaction phenomenon in polynuclear complexes has been achieved in the last few years.[1] In particular, the different orbital models recently proposed have allowed appreciation of the main structural factors governing the sign and magnitude of the exchange interaction.[2-3] In these models, the J triplet–singlet energy gap characterizing the exchange interaction in copper(II) dinuclear complexes is generally expressed as the sum of a negative component, J_{AF}, and a positive component, J_F. J_{AF} and J_F related to the overlap integral and the two-electron exchange integral between the magnetic orbitals, respectively, are both very sensitive to small structural modifications.[4] In the quasi-totality of the Cu(II) dinuclear complexes studied so far, the presence of bridging ligands between the metallic centers leads to a great rigidity of the molecular edifice so that J is essentially independent of the temperature.[5] A unique value of J may be deduced from the variation of the magnetic susceptibility against the temperature. If, on the contrary, the binuclear complex has a structure possessing some flexibility, a temperature dependence of J may be expected. Dinuclear cryptates obtained by inclusion of two metallic ions into the intramolecular cavities containing two cation binding subunits[6] may be good candidates to observe such a phenomenon, which we propose to name *exchange elasticity*. The crystal and molecular structure of a complex of this type, prepared earlier,[6] is $[Cu^{II}_2 \subset (C_{24}H_{48}N_4O_2S_4)](ClO_4)_4(H_2O)$ (I), where the cryptand is 1,7,13,19-tetraaza-4,16-dioxa-10,22,27,32-tetrathiatricyclo[17.5.5.5^{7,13}]tetratriacontane. This structure is shown in Figure 1.[7] The magnetic properties of I are given in Figure 2 under the form of the variations of the molar magnetic susceptibility, χ_M, and the product $\chi_M T$ vs. the temperature T.[8] Examination of this latter plot leads to the following observations: (i) Although the Cu–Cu intracavity distance is 5.62 Å, the exchange interaction of antiferromagnetic nature appears surprisingly strong. When I is cooled below room temperature, $\chi_M T$ continuously decreases. (ii) Below 50 K, the variation of $\chi_M T$ is linear and follows the equation $\chi_M T/\text{cm}^3\ \text{mol}^{-1}\ \text{K} = 0.00740\ T/\text{K} + 0.0713$. This behavior does not correspond at all to eq 1, which gives the magnetic susceptibility for a Cu(II) dimer in which a proportion,

$$\chi_M = \frac{2N\beta^2g^2}{kT}\left[3 + \exp\left(-\frac{J}{kT}\right)\right]^{-1}(1-\rho) + \frac{N\beta^2g^2}{2kT}\rho \quad (1)$$

ρ, of noncoupled Cu(II) as an impurity is taken into account. From eq 1, $\chi_M T$ at very low temperatures should approach a constant and very weak value, corresponding to the ρ proportion of noncoupled Cu(II). Such a low-temperature behavior fitting eq 1 has been obtained for all the Cu(II) dinuclear complexes studied in our laboratory.[9] In other respects, the molecular packing is such that the intermolecular interactions should be negligible and may not explain in any way the observed behavior with the complex I. Indeed the shortest intermolecular Cu–Cu distance is about 8.2 Å, and the two nearest neighbor cryptate units are separated by noncoordinated perchlorate anions.[10]

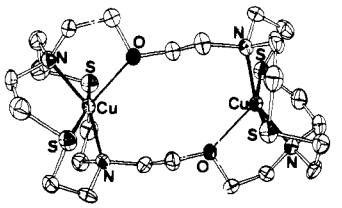

Figure 1. Molecular structure of the cryptate complex $[Cu^{II}_2 \subset (C_{24}H_{48}N_4O_2S_4)]^{4+}$.

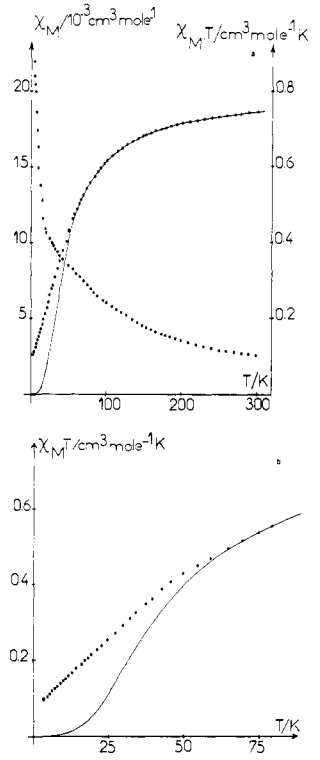

Figure 2. Experimental temperature dependence of χ_M and $\chi_M T$ for complex I. Curve deduced from eq 1 with $J = -56.7$ cm^{-1}, $g = 2.071$, and $\rho = 0$ (see text). (a) Temperature range 4–300 K; for clarity, the experimental points below 30 K have not all been indicated. (b) Temperature range 4–75 K.

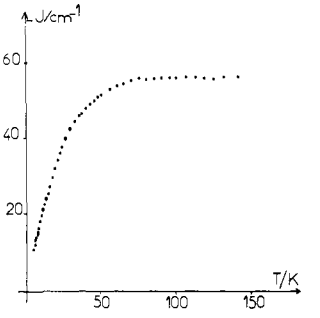

Figure 3. Temperature dependence of J on complex $[Cu^{II}_2\text{-}H \subset (C_{24}H_{48}N_4O_2S_4)]^{4+}$.

(1) See, for example: S. L. Lambert and D. N. Hendrickson, *Inorg. Chem.*, **18**, 2687 (1979), and the previous papers of the same series; C. Chauvel, J. J. Girerd, Y. Jeannin, O. Kahn, and G. Lavigne, *ibid.*, **18**, 3015 (1979), and references therein; O. Kahn, P. Tola, J. Galy, and H. Coudanne, *J. Am. Chem. Soc.*, **100**, 3931 (1978); V. H. Crawford, H. W. Richardson, J. R. Wasson, D. J. Hodgson, and W. E. Hatfield, *Inorg. Chem.*, **15**, 2107 (1976), and references therein.

(2) P. J. Hay, J. C. Thibeault, and R. Hoffmann, *J. Am.* Chem. *Soc.*, **97**, 4884 (1975).

(3) O. Kahn and B. Briat, *Colloq. Int. C.N.R.S.*, **no. 255**, 251 (1976); J. J. Girerd, M. F. Charlot, and O. Kahn, *Mol. Phys.*, **34**, 1063 (1977), M. F. Charlot, S. Jeannin, Y. Jeannin, O. Kahn, J. Lucrece-Abaul, and J. Martin-Frere, *Inorg. Chem.*, **18**, 1675 (1979).

(4) O. Kahn and M. F. Charlot, *Nouv. J. Chim.*, in press.

(5) A nice experimental demonstration of a small temperature dependence of the singlet–triplet energy gap in a Cr(III) dinuclear complex has been given by H. U. Gudel and A. Furrer, *Mol. Phys.*, **33**, 1335 (1977).

(6) A. H. Alberts, R. Annunziata, and J. M. Lehn, *J. Am. Chem. Soc.*, **99**, 8502 (1977), and references therein.

(7) R. Louis, Y. Agnus, and R. Weiss, *J. Am. Chem. Soc.*, **100**, 3604 (1978).

(8) The magnetic measurements were carried out on two samples of about 8 mg each, obtained from different preparations. The sample leading to the data of Figure 1 was obtained by picking up some rather large single crystals under a binocular lens. The results of two experiments were identical within the experimental uncertainties (0.1 K on the temperature and 15×10^{-6} cm^3 mol^{-1} on the susceptibility). The measured susceptibilities were corrected for the temperature-independent susceptibility, including the diamagnetism and the TIP. This correction was estimated at -505 cm^3 mol^{-1}.

(9) See, for example; in addition to the papers already cited in ref 1 and 3: J. J. Girerd, S. Jeannin, Y. Jeannin, and O. Kahn, *Inorg. Chem.*, **17**, 3034 (1978); J. Galy, J. Jaud, O. Kahn, and P. Tola, *Inorg. Chim. Acta*, **36**, 229 (1979); also several unpublished results.

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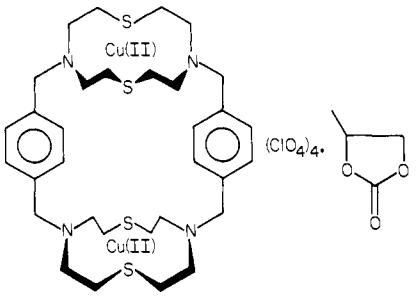
From a quantitative point of view, between 300 and 55 K, the magnetic susceptibility very closely follows eq 1 with $J = -56.7$ cm^{-1}, $g = 2.071$, and ρ negligible (see Figure 2).[11] Below 55 K, the experimental data drastically deviate from eq 1 when J is assumed to be constant in the whole temperature range. By determining the g and ρ values at high temperatures and allowing J to vary, one obtains the temperature dependence of J plotted in Figure 3. The singlet–triplet energy gap is essentially constant down to 55 K, then decreases more and more quickly as the temperature drops below 55 K.[12] The temperature dependence of the intensity of the $\Delta M_S = \pm 1$ ESR transition in the range 10–300 K nicely confirms this result.

The same phenomenon of exchange elasticity seems to occur, but in a less spectacular manner, in compound II, $[Cu^{II}_{27} \subset (C_{32}H_{48}N_4S_4)](ClO_4)_4(C_4H_6O_3)$, the exact molecular structure of which has not yet been determined.[13] Down to 14K, the



II

magnetic susceptibility fits eq 1 for $J = -8.39$ cm^{-1}, $g = 2.184$, and $\rho = 0.0258$.[14] Below 14 K, the magnetic data very strongly suggest a gradual decrease of $|J|$, down to a value of about 4.8 cm^{-1} at 4 K.

The mechanism of the exchange in complex I is in itself an interesting problem. Each Cu(II) ion is surrounded by a strongly distorted tetragonal pyramid in which the metal lies 0.34 Å above the N_2S_2 basal plane toward the axial oxygen atom. This large displacement of the Cu(II) ion out of the N_2S_2 plane indicates that the axial Cu–O interaction is much more important than in most of the Cu(II) complexes with a 4 + 1 coordination.[15] Consequently, the metallic contribution to the magnetic orbital around each Cu(II) ion may not be reduced to $d_{x^2-y^2}$ pointing toward the sulfur and nitrogen atoms but has a d_{z^2} axial component so that the spin density on the oxygen atom is nonnegligible. The exchange interaction between the two chromophores CuS_2N_2O in the cavity has three preferential pathways: once Cu–O···O–Cu and twice Cu–N–CH_2–CH_2–O–Cu. The efficiency of each of these pathways is related to the spin density on the oxygen atoms in the chromophores CuN_2S_2O. One conceives that a slight displacement of the copper toward the basal plane at low temperature or an increase of the angle between the Cu–O bond and the z axis perpendicular to the basal plane might lead to a very sensitive lessening of the spin density on the oxygen atoms, hence to a weakening of the antiferromagnetic interaction inside the cavity. This phenomenon of exchange elasticity could also be of the same nature as the exchange striction introduced by the solid-state physicists,[17] but largely enhanced here owing to the quite specific nonrigidity of the cryptate cavity.

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(10) R. Weiss, private communication.
(11) The agreement factor R defined as $\sum(\chi_M^{obsd} - \chi_M^{cald})^2/\sum(\chi_M^{obsd})^2$ is then equal to 0.35×10^{-4}.
(12) The $g_{\parallel}$ and $g_{\perp}$ factors deduced from the ESR spectra are essentially independent of the temperature in the range 10–300 K. If a small proportion, ρ, of paramagnetic impurity which would not have been detected from the experimental data in the 55–300 K range was present, the actual slope of the $|J|$ vs. T plot would be slightly weaker than it is shown in Figure 3.
(13) The ligand has been synthetized by Dr. J. Rimmer; unpublished results.
(14) The agreement fractor R is 0.52×10^{-4}.
(15) See, for example: B. J. Hathaway, *Struct. Bonding (Berlin)*, **14**, 49 (1973).
(16) On the concept of magnetic orbitals, see ref 3 and 4.
(17) M. E. Lines, *Solid State Commun.*, **11**, 1615 (1972), and references therein; J. Katriel and O. Kahn, Phys. Lett. *A*, **55A** 439 (1976).
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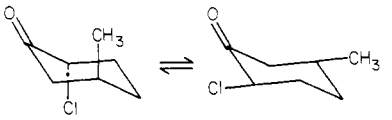
Water Penetration into Micelles as Determined by Optical Rotary Dispersion

Sir:

We have recently questioned the classical Hartley model[1] which portrays micelles as "oil droplets" encased by ionic shells.[2] In particular, we have supplied evidence that water penetrates deeply into the aggregates and that the so-called Stern layer is rough and poorly defined.[3-5] Our "porous-cluster" description has not achieved universal acceptance, however, as shown by a recent editorial in opposition to it.[6] The venerable Hartley model is obviously difficult to abandon because, for one thing, its deceptive simplicity facilitates theoretical calculations. Moreover, experiments designed to define the structure of transient aggregates in solution necessarily entail assumptions and limitations that preclude "proof" in the usual sense of the word. Presented below are optical rotary dispersion data which strongly support the presence of water inside micelles. To our knowledge, this is the first time that ORD has been applied to micellar structure.

Transferring (+)-*trans*-2-chloro-5-methylcyclohexanone from heptane to water induces a remarkable change in the sign of the Cotton effect (Figure 1, A and B).[7] This can be ascribed to a



heptane water

diaxial–diequatorial equilibrium which lies further to the right in water than in heptane.[8] The conformationally mobile ketone thus responds to the nature of the medium and can be used as a sensitive probe of micellar environments. The RD curves of 6.8 $\times 10^{-3}$ M probe in aqueous surfactant solutions composed of 0.10 M hexadecyltrimethylammonium bromide (HTAB) or 0.10 M sodium dodecyl sulfate ($NaDodSO_4$) are shown in Figure 2, A and B, respectively. It is seen that (+)-*trans*-2-chloro-5-methylcyclohexanone in the micellar solutions gives a Cotton effect similar to that in pure water. The following observations leave no doubt that the probe does in fact adsorb into or onto the micelles: (1) One can readily dissolve 0.005 M ketone in 0.20 M $NaDodSO_4$ with brief shaking whereas dissolution in pure water requires sonication. (2) The partition coefficient of the probe between heptane and water ($K_{H/W}$) equals 5.5. Adding 0.10 M $NaDodSO_4$ to the water decreases $K_{H/W}$ to 1.5, thereby proving

(1) D. Stigter, *J. Phys. Chem.*, **78**, 2480 (1974).
(2) P. Mukerjee and J. R. Cardinal, *J. Phys. Chem.*, **82**, 1620 (1978).
(3) F. M. Menger, *Acc. Chem. Res.*, **12**, 111 (1979).
(4) F. M. Menger, J. M. Jerkunica, and J. C. Johnston, *J. Am. Chem. Soc.*, **100**, 4676 (1978).
(5) F. M. Menger, *J. Phys. Chem.*, **83**, 893 (1979).
(6) H. Wennerström and B. Lindman, *J. Phys. Chem.*, **83**, 2931 (1979).
(7) All spectra were secured with the aid of a Perkin-Elmer 241 MC polarimeter and 10-cm quartz ORD cells thermostated at 25.0 °C.
(8) C. Djerassi, L. E. Geller, and E. J. Eisenbraun, *J. Org. Chem.*, **25**, 1 (1960).
(9) This increase in rotation implies that the micelle environment, although aqueous, is different from that of bulk water (as would be expected from a micelle bearing aqueous pockets). Note that Na_2SO_4 (1.0 M) does *not* induce a similar rotation increase with the aqueous probe. Ketone (0.005 M) will not dissolve in 2.0 M Na_2SO_4 at 25 °C.

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