Table II

Starting porphyrin	K, 10^{-4} min^{-1}	$t_{1/2}$, min
$Co^{III}Br(NH_3)$ Aetio I[a]	670 ± 60	10.5 ± 0.6
$Co^{II}OEP$	300 ± 20	23 ± 2
Aetio I	69 ± 2	101 ± 2
OEP	50 ± 5	140 ± 14
$Fe^{III}ClOEP$[a]	3.0 ± 0.15	2300 ± 100

[a] In acetic acid $Co^{III}Br(NH_3)$ Aetio I porphyrin is immediately converted into the corresponding $Co^{III}Br$ Aetio I. Both the $Co^{III}Br$ Aetio I and $Fe^{III}ClOEP$ porphyrins can be recovered unchanged from refluxing acetic acid.

between these rates and either the presence or absence of metal, or the oxidation state of the metal. Also, contrary to prior reports,[4] we find that Co(III) porphyrins not only exchange, but do so faster than any of the other porphyrins examined.

It had been suggested[8] that the meso positions of metal-free porphyrins would resist attack by electron-deficient reagents, and no change in the nmr spectrum of rhodoporphyrin dimethyl ester was observed when it was treated with deuterioacetic acid at 90° for 5 hr. However, we find that metal-free porphyrins exchange at a rate comparable to the metalloporphyrins in refluxing deuterioacetic acid. Under these conditions, OEP exists 60% as the N-diprotonated species, and 40% as the neutral porphyrin. In DTFA, where the concentration of neutral porphyrin is negligible, the rate of exchange is very much slower, and it is clear that N-protonation accounts for the previously observed deactivation of metal-free porphyrins in strong acids, and that it is the neutral porphyrin which undergoes electrophilic attack. The absence of exchange with rhodoporphyrin in deuterioacetic acid is not a basic property of metal-free porphyrins, and is probably a function of the electron-withdrawing methoxycarbonyl group. The dicyano–Co(III) complex showed a rate of deuteration which increased with time, but which remained slower than the corresponding amino–bromo complex. It has been reported[9] that refluxing acetic acid converts the dicyano into the monocyano complex, and thus we conclude that the rate of electrophilic attack on a porphyrin is dependent not only upon the nature of the metal (and its oxidation state), but also upon the nature of the axial ligands.

It was recently suggested[10] that a small incorporation of deuterium into the meso positions of an Fe(III) porphyrin during its reduction, by iron powder in deuterioacetic acid–*N*-methylpyrrolidone, gave *direct* evidence for peripheral attack on the metalloporphyrin during chemical reduction. While peripheral attack on porphyrins is undoubtedly an important aspect of both their chemistry and biochemistry,[11] the 5% deuterium incorporation observed during the reduction could also be explained by an electrophilic attack on the Fe(II) complex which is isoelectronic with the cobalt(III) complex (the fastest reacting example we have observed).

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Spin–Spin Coupling between Copper(II) Ions Bridged by Pyrazine Ligands

Sir:

The magnetic properties of the 1:1 copper(II) nitrate–pyrazine complex, $[Cu(C_4N_2H_4)(NO_3)_2]_n$, reflect an exchange coupling between the copper ions although, as shown schematically in Figure 1, the copper(II) ions are separated by 6.712 Å.[1] While exchange coupling across bidentate heterocyclic amine ligands has been suggested previously,[2] these results provide the first demonstration of an antiferromagnetic interaction in a system which has been characterized by structural studies, magnetic measurements collected over a wide temperature range, and epr measurements.

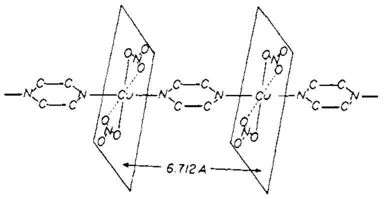

Figure 1. The structure of $[Cu(C_4H_4N_2)(NO_3)_2]_n$.

The magnetic susceptibility of a powdered sample of an analytically pure sample was determined in the temperature range 2.9–65°K using a vibrating sample magnetometer[3,4] operated at 10,000 G and calibrated with $Hg[Co(NCS)_4]$.[5] Temperatures were measured with a calibrated germanium resistance thermometer using a high-impedence ac resistance bridge, and with a gallium arsenide diode. Appropriate diamagnetic and TIP corrections[6] were applied to the experimental data. The data can be described by the Ising model for linear antiferromagnetic interactions in chains using eq 1 developed by Fisher.[7]

The equations are

$$\chi_{\perp} = \frac{Ng^2\beta^2}{8J}\left[\tanh\left(\frac{J}{kT}\right) + \left(\frac{J}{kT}\right)\operatorname{sech}^2\left(\frac{J}{kT}\right)\right] \qquad (1a)$$

and

$$\chi_{\parallel} = \frac{Ng^2\beta^2}{4kT}\exp(2J/kT) \qquad (1b)$$

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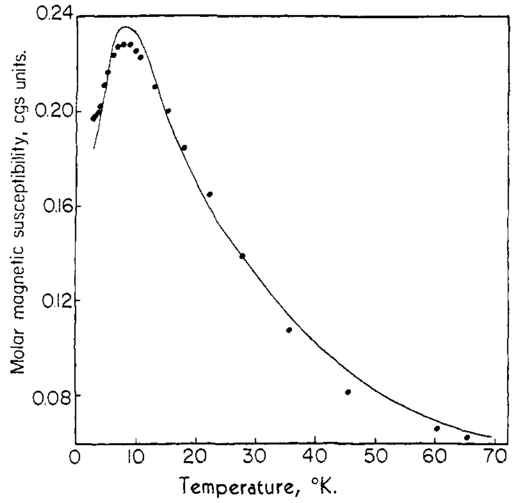

Figure 2. The temperature dependence of the magnetic susceptibility of $[Cu(C_4H_4N_2)(NO_3)_2]_n$. The experimental data (●) are compared to the best fit to the Ising model with $J = -6.0$ cm^{-1} and $\langle g \rangle = 2.22$.

where

$$\langle \chi \rangle = \frac{1}{3}\chi_{\parallel} + \frac{2}{3}2\chi_{\perp}$$

The parameters which give the best fit to the experimental data shown in Figure 2 are $\langle g \rangle = 2.22$ and $J = -6.0$ cm^{-1}.

The best-fit $\langle g \rangle$ value is to be compared with the epr results of Kokoszka and Reimann,[8] who reported $g_z = 2.295$, $g_x = 2.054$, and $g_y = 2.070$ ($\langle g \rangle = 2.133$). They differ by about 0.09 unit. Furthermore, if the presumably more precise epr $\langle g \rangle$ value of 2.133 is used in the calculations, the best-fit J value changes only slightly, to -5.3 cm^{-1}, even though the fit is about four times poorer. This is indicative of the correctness of the calculated J value. The deviation suggests that the Heisenberg model may be more appropriate, since Bonner and Fisher[9] have shown that the susceptibility variation with temperature for this model exhibits more rounded cusps than the Ising model. Measurements on single-crystal samples will permit the selection of the appropriate model.

Additionally, it is important to note that a distinct absorption in the epr spectrum at $g = 3.97$ was observed using an E-3 spectrometer at 9.180 GHz. Although half-field absorptions are sometimes seen for pure powdered samples of copper dimers,[10] such features are rarely observed for polymeric materials.

Owing to the highly unusual structural features of this molecule, the unpaired electron in the σ-antibonding level of the copper ion may interact with the π electrons of the aromatic heterocyclic amine, thus effecting an antiferromagnetic interaction by a superexchange mechanism. Never before have copper ions so far removed from one another been observed to be exchange coupled with an interaction constant of the magnitude of that observed here. Furthermore, these results reflect the importance of the consideration of interactions among the unpaired spins when interpreting magnetic and epr data in systems where the metal ions are far apart.

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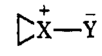
Rearrangement of Strained Dipolar Species, Aziridine *N*-Oxides. II[1]

Sir:

In a study of the chemistry of strained dipoles, exemplified by the general expression **1**, we were recently



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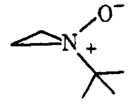

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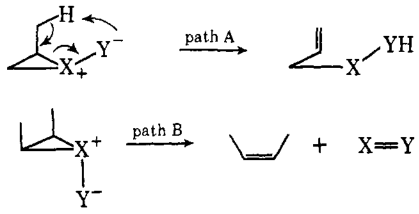
able to elucidate the two pathways involved in the decomposition of episulfoxides (**1**, X = S; Y = O), namely a ring opening with concerted hydrogen shift, path A, and a less facile and partially stereospecific ejection of the elements of XY, path B, when the stereochemistry is not favorable for the hydrogen-transfer reaction. We now report on the aziridine *N*-oxides (**1**, X = NR; Y = O). Although such species have been postulated as intermediates in certain oxidations of aziridines,[2,3] they have until now eluded detection, and our own studies, which have revealed these species for the first time, amply justified the prior intimations of instability.



Ozonolysis of *N*-*tert*-butylaziridine at −75° in methylene chloride (3 g/100 ml) provided a solution of *N*-*tert*-butylaziridine *N*-oxide (**2**)[4] stable up to 0°. Examination of the nmr spectrum[5] of this solution at temperatures up to 0° showed a new *tert*-butyl absorption, δ 1.22 (s, 9 H), and the methylene protons as an A_2B_2 multiplet centered at 2.6 (m, 4 H), significantly shifted downfield from the starting material, 0.80 (s, 9 H), 1.30 (m, 4 H). Above 0° this substance smoothly underwent first-order decomposition into eth-

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[5] All low-temperature nmr studies were conducted in a Varian HA-100 spectrometer fitted with a variable-temperature probe.