cyclopropenyl ring with a suitable nickel hybrid orbital (d_{z^2}, s and p_z contribution) and (2) interaction of the a_1 and e_1 combinations (C_{5v} localized symmetry) of the $p\pi$ orbitals on the cyclopentadienyl ring with an a_1 and e_1 set on the nickel atom.

Nickel complex **7**, like the isoelectronic cobalt analog **5**,[6] might be expected to undergo various aromatic-type ring substitution reactions, and studies along these lines are currently in progress.

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Triplet Ground State in the Dimer Bis(pyridine *N*-oxide)copper(II) Nitrate

Sir:

While there are great numbers of dimeric copper(II) complexes which exhibit low magnetic moments as a result of electronic spin–spin coupling giving singlet ground states,[1] there have been, up to now, no well-documented examples of copper dimers with triplet ground states. There are at least two reasons for the absence of examples of copper(II) dimers with triplet ground states. First, owing to the irregularities in the structure of copper(II) complexes, few adjacent copper ions have their unpaired electrons in orthogonal interacting orbitals as required for triplet ground states. The negative terms in the expression for the exchange coupling constant, J, are weighted by the overlap integral, S, and will disappear when the overlap integral is zero. The remaining positive term is not multiplied by S.[2] In addition to the potentially fewer numbers of copper dimers with $+J$, the probability of finding examples is diminished by the experimental difficulties which are present. First, copper complexes with "normal" moments do not attract much attention, and consequently crystallographers have not provided much structural information on dimeric copper complexes with "normal" moments. Secondly, only low-temperature magnetic susceptibility measurements and electron paramagnetic resonance experiments will provide the necessary documentation.

We have been systematically searching for copper dimers with triplet ground states and present electron spin resonance and static magnetic susceptibility data here which indicate that the electronic spin–spin interaction in the dimeric molecule bis(pyridine *N*-oxide)-copper(II) nitrate yields a triplet ground state. The crystal structure of $[Cu(C_5H_5NO)_2(NO_3)_2]_2$, schematically shown in Figure 1, has been determined by Šćarničar and Matković.[3] Each copper ion is in a tetragonal pyramidal environment with trans pyridine *N*-oxide molecules and nitrate groups in the plane of the pyramid, and with an oxygen from a pyridine *N*-oxide in the plane of the neighboring copper ion occupying the fifth coordination position at the apex of the pyramid.

We have measured the magnetic susceptibility of a sample[4] of this compound in the range 2.4–300°K with a Foner-type[5] vibrating sample magnetometer[6] and a Faraday balance.[7] The data obey the Curie–Weiss law with a value for C of 0.449 emu deg mol^{-1}, which yields a magnetic moment of 1.90 BM per copper(II) ion. The intercept of the temperature axis at $\chi^{-1} = 0$ is $+2$°K. The magnetic data can be described in terms of the Van Vleck equation (1) for exchange-coupled pairs of copper ions with $J \sim 15$ cm^{-1} and $\langle g \rangle = 2.11$. Unfortunately, the calculated

$$\chi_m = \frac{g^2 N\beta^2}{3kT}\{1 + {}^1/_3 \exp(-2J/kT)\}^{-1} \qquad (1)$$

susceptibilities are not very sensitive to the choice of J, but the value obtained here is in good agreement with that estimated from the electron spin resonance data given below. The discrepancy between observed and calculated susceptibilities for small negative values of J was markedly greater than that of the assigned value of J.

The epr spectrum at 300° of a powdered sample of $[Cu(C_5H_5NO)_2(NO_3)_2]_2$ yields one broad line centered at 3100 G. At 77° additional lines, one at 3067 G and a less intense line at $\sim$1500 G due to the $\Delta M_s = \pm 2$ transition,[8] can be resolved. There is no further change in the spectrum at 4.2°K. However, the epr spectrum of a magnetically dilute sample prepared by substituting zinc ions for copper[9] provides the most convincing evidence for the triplet state. The sample was prepared by mixing 2,2-dimethoxypropane solutions of copper(II) nitrate and zinc nitrate in the molar ratio of 1:9 and the stoichiometric amount of pyridine *N*-oxide. At 77°K a powdered sample gives an epr spectrum with a very intense absorption near 3050 G on which the expected copper hyperfine structure is seen. On the low-field side, the separation between these components is 90 G. This absorption arises from copper ions in spin state $S = {}^1/_2$ which are present in dimeric molecules with neighboring zinc ions, *i.e.*, in $[Zn(Cu)(C_5H_5NO)_4(NO_3)_4]$. In addition to the intense absorption at 3050 G, as shown in Figure 2,

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[4] *Anal.* Calcd for $Cu(C_5H_5NO)_2(NO_3)_2$: C, 31.80; H, 2.67; N, 14.83. Found: C, 31.79; H, 2.71; N, 14.85.

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[8] All line positions have been adjusted to be correct for a frequency of 9.182 GHz.

[9] The X-ray powder patterns of $[Cu(C_5H_5NO)_2(NO_3)_2]_2$ and the solid solution are nearly identical. *Anal.* Found for $[Cu(Zn)(C_5H_5NO)_2(NO_3)_2]_2$: C, 31.95; H, 2.61; N, 14.80.

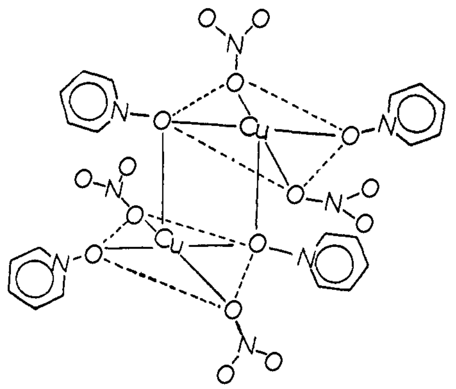

Figure 1. The structure of dimeric bis(pyridine *N*-oxide) copper(II) nitrate.

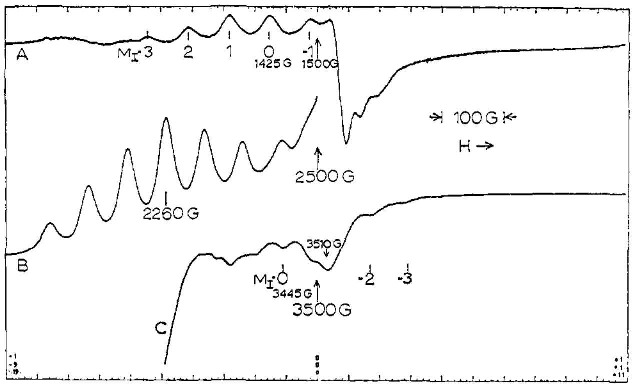

Figure 2. The epr spectrum of $[Zn(Cu)(C_5H_5NO)_2(NO_3)_2]_2$ showing the regions (a) 1000–2000 G, (b) 2000–3000 G, (c) 3000–4000 G. The spectra were recorded at 77 °K.

there are much less intense absorptions near 1425, 2260, 3445, and 3510 G. These four lines arise from the triplet-state molecules $[Cu(C_5H_5NO)_2(NO_3)_2]_2$ which are expected to be present in a much lower concentration than the $S = {}^1/_2$ species. Although it is unlikely that the g and hyperfine tensors are coincident, the spectrum has been tentatively interpreted in terms of the spin Hamiltonian (2) for the triplet state.[10] A more complete description of the magnetic resonance must await additional data.

$$\mathcal{H} = \beta HgS + DS_z^2 + E(S_x^2 - S_y^2) - {}^2/_3D \quad (2)$$

The H_{min} absorption[11] near 1425 G due to the $\Delta M_s = 2$ transition shows considerable hyperfine structure although the seven expected lines were not resolved. The splitting which can be measured between adjacent lines on the low-field side is 64 G. Copper hyperfine lines can also be detected on the absorption at 2260 G, where the separation is also approximately 64 G. This absorption is assigned to the low-field parallel transition as designated by Wasserman, *et al.*,[12] and is indicative of a low zero-field splitting parameter, D. Unfortunately, the absorptions, on the high-field side of the $S = {}^1/_2$ spectral lines, could not be measured with much precision at x band (9.182 GHz) since they are on the tail of the much more intense absorption due to copper ions with $S = {}^1/_2$.

The absorption at 3445 G is due to the $M_I = 0$ component of the high-field parallel transition and with this assignment the absorption at 3510 G arises from the high-field perpendicular transition. The absence of hyperfine structures on the 3510-line and the presence of the $M_I = -3, -2$ components of the high-field parallel line as shown in Figure 2 confirm these assignments. This gives $g_{xy} = 2.05$, $g_z = 2.23$, $|D| = 0.062 \pm 0.001$ cm^{-1}, and with these values the low-field perpendicular component is calculated to be at 2863 G. This transition is in the region of the $S = {}^1/_2$ species, but there is a suggestion of a line at this field value. Assignment of the absorptions to other transitions leads to unlikely magnetic parameters.

The exchange coupling constant can be roughly approximated by an analysis of the contributions to the zero-field splitting parameter D. From the point charge model, the dipole–dipole contribution is calculated to be 0.08 cm^{-1}. Since $D = D_{dipole} + D_{exchange}$, then $|D_{ex}| = 0.02 - 0.14$ cm^{-1}, and by application of the Bleaney–Bowers approximation,[10,13] then $2J = 10$–100 cm^{-1}. The agreement of J which results from this analysis, augmented by the value for this parameter obtained from the susceptibility data, strongly supports the conclusion that $[Cu(C_5H_5NO)_2(NO_3)_2]_2$ has a triplet ground state and discounts the possibility that the ground state is a singlet with the triplet state lying very low. All attempts to grow single crystals of the copper–zinc dilute material for more careful measurements have been unsuccessful. Spectrometers with other radiation frequencies are being assembled for additional experiments.

We believe that the dimeric molecule $[Cu(C_5H_5NO)_2(NO_3)_2]_2$ represents the first authenticated example of exchange-coupled copper(II) ions with a triplet state ground state. On the basis of less complete information, Rundle and coworkers[17] have suggested a triplet ground state for the planar $Cu_2Cl_6^{2-}$ ion in $LiCuCl_3 \cdot 2H_2O$, but newer more complete data[18] have shown the system to have a singlet ground state. Previous statements[3] concerning the absence of spin–spin coupling in $[Cu(C_5H_5NO)_2(NO_3)_2]_2$ must be viewed in historical perspective. The exchange coupling is a σ-orbital mechanism which is transmitted through the orbitals of the bridging oxygen atoms by electron transfer plus intraatomic direct exchange.[19]

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New Theoretical Evidence for the Nonlinearity of the Triplet Ground State of Methylene

Sir:

It is generally accepted[1] that the triplet ground state of the CH_2 molecule is linear. However, it is interesting to note that both Walsh,[2] in his early qualitative paper, and Herzberg,[3] in his experimental study, leave open the possibility that this state is "nearly linear." Further, early *ab initio* configuration interaction (CI) calculations by Foster and Boys[4] indicated a relatively flat surface with changing angle and an equilibrium angle of 129°. Finally, from recent valence-bond calculations, Harrison and Allen[5] predicted an angle of 138° for the ground $^3B_1$ state.

We have recently begun a relatively accurate series of quantum mechanical calculations on the low-lying states of the CH_2 radical. It was decided to first investigate the question of the geometry of the ground state.

The gaussian basis functions used in this work were Huzinaga's[6] 9s,5p set for carbon and 4s set for hydrogen. The functions were contracted to 4s,2p for carbon and 2s for hydrogen (with a scale factor of 1.2), according to Dunning's recommendations.[7]

The first step in each calculation involved the computation of the SCF wave function within the above basis. Then CI calculations were carried out including the SCF function ($1a_1^2\ 2a_1^2\ 1b_2^2\ 3a_1\ 1b_1$ in this case) plus all configurations of $^3B_1$ symmetry arising from orbital occupancies differing by one or two orbitals from the SCF function, with the restriction that the $1a_1$ orbital was always doubly occupied. An iterative natural orbital procedure[8] was then used in several subsequent CI calculations to obtain the most rapidly convergent expansion of the above type. Calculations were also routinely carried out for SCF plus single excitations only.

We carried out a much more exhaustive geometry search than previous *ab initio* investigators[4,5,9] of CH_2. The calculated total energies from our largest calculation (including 408 $^3B_1$ configurations) are given as a function of geometry in Table I. Our lowest calculated total energy lies 0.0671 hartree = 42 kcal/mol below the lowest energy previously reported, that of Harrison and Allen.[5] Force constants were obtained by fitting the expression[10]

Table I. Calculated *Ab Initio* Energies for the Ground $^3B_1$ State of CH_2[a]

	R, bohrs			
θ	1.9	2.0	2.1	2.2
90°	−38.92913	−38.94283	−38.94751	−38.94554
105°	−38.95363	−38.96588	−38.96916	−38.96583
120°	−38.96644	−38.97761	−38.97986	−38.97554
135°	−38.97045	−38.98077	−38.98222	−38.97717
150°	−38.96881	−38.97838	−38.97912	−38.97344
165°	−38.96527	−38.97413	−38.97425	−38.96799
180°	−38.96347	−38.97200	−38.97184	−38.96530

[a] The wave functions were of the configuration-interaction variety, including the SCF function plus all singly and doubly excited configurations arising from a "double-ζ" gaussian basis set. In all, 408 configurations were included.

$$2V = F_{11}r_1^2 + F_{22}r_2^2 + F_{33}R^2\alpha^2$$

where r_1 and r_2 are the stretches of the two CH bonds, α is the distortion of the equilibrium bond angle, and R is the equilibrium bond length. Table II gives the predicted geometry and force constants for each of the three types of calculation carried out.

Table II. Predicted Equilibrium Geometry and Force Constants (mdyn/Å) of CH_2

	SCF	SCF + single excitations	SCF + single excitations + double excitations	Experiment[a]
Bond distance, Å	1.080	1.080	1.096	1.03
Bond angle, deg	129.8	135.7	135.1	180
Interpolated total energy, hartrees	−38.913	−38.921	−38.984	
$F_{11} = F_{22}$	6.41	6.52	6.83	
F_{33}	0.26	0.20	0.21	

[a] See ref 3.

All the present calculations indicate that the methylene ground state is bent, with a bond distance greater than the 1.03 Å determined by Herzberg.[3] In light of the present results it is interesting to note that an alternate interpretation[3] of Herzberg's spectroscopic data suggested a bond distance of 1.071 Å and a 140° angle, in good agreement with our predictions. However, owing to the absence in the spectrum of certain subbands, Herzberg[3] concluded the above geometry to be unlikely. The fact that the potential surface is rela-

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