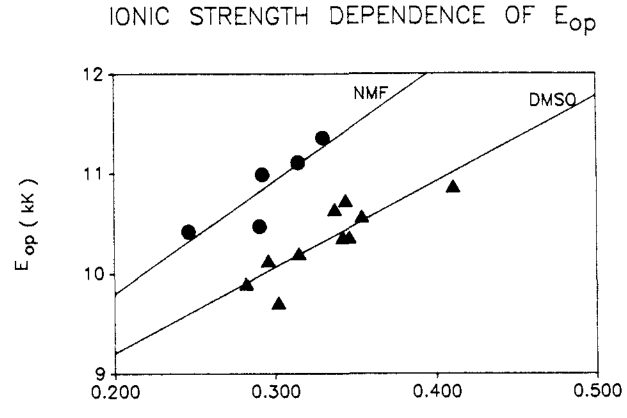

Figure 1. Modified Debye–Huckel plot for intervalence transition band energies of complex I in dimethyl sulfoxide (triangles) and *N*-methylformamide (circles).

computer-generated least-squares fits to the data. It is apparent that the energies of the IT bands in these solvents extrapolated to zero ionic strength (7.49 in dimethyl sulfoxide and 7.54 kK in *N*-methylformamide, a difference of only 0.7%) were essentially identical within experimental error, whereas the energies at any other value of the ionic strength differed by a measureable amount. For example, without any added salts, a common way of performing these experiments, the corresponding values were 9.90 and 10.4 kK, a difference of 5.1%. There was no systematic change in the peak shape or width as a function of ionic strength. The average value of the full-width at half-height was 7.6 ± 0.2 kK in *N*-methylformamide, whereas it was 6.2 ± 0.8 kK in dimethylformamide.

In the usual theoretical treatments[6-11] of electron-transfer reactions, no specific ion-pairing interactions are assumed. The theories also usually assume that the solvent forms a dielectric continuum around the reacting species although this is known[1,12-14] to be a poor approximation. Noncontinuum effects have recently been shown to overwhelm the dielectric continuum effects, especially in ruthenium ammine complexes.[1] In the absence of high concentrations of ions, specific solute–solvent interactions are the main sources of these noncontinuum effects, via hydrogen bonding interactions. In the presence of suitable concentrations of oppositely charged ions, under conditions typical of those employed to run IT bands, ion pairs become possible. There is thus a competition between the solvent and anions (or cations) to complex with the cationic (or anionic) binuclear species in solution. The extent of ion pairing that results depends inversely on the dielectric constant of the solvent, directly on the charges of the ions involved, and directly on the concentrations of the ions.

The effect of the ion pairing on the potential energy surface may be rationalized in terms of the polarization around the binuclear, $\vec{P}(\vec{r})$. The ground-state potential energy surface may be expressed as a functional of this polarization, $F[\vec{P}(\vec{r})]$. Thus, $F[\vec{P}(\vec{r})]_0$, the ground-state potential surface, may be defined by specific solute–solvent interactions at zero ionic strength. The surface so defined becomes perturbed in the presence of appreciable quantities of anions, as atmospheric condensation ensures.[15] The ground-state potential energy surface experiences a stabilization as a result of this perturbation, i.e.,

$$E_{op}(\mu) = E_{op}{}^{\circ} + \Delta G(\mu)$$

Although the ion pairing stabilizes the ground-state equilibrium potential energy surface, the excited state surface does not necessarily experience a corresponding stabilization. The lifetime of the excited state is relatively short compared with the time required to reorganize the ion pair into an equilibrium configuration compatible with the new electronic state. Consequently, the separation between the ground state and the excited state potential energy surfaces tends to widen as the ionic strength of the medium increases. This leads to the observed increase in E_{op} with increasing ionic strength.

In an interesting paper concerning measurements of IT bands in several frozen solvents under pressure at 25 °C, Drickamer et al.[16] determined that there was essentially no change in peak maxima in going from the liquid to the solid state although the static dielectric constant changed by almost a factor of 10 under the same conditions. From these observations, they concluded, and the conclusion is further reinforced in the present paper, that the dielectric continuum model was inadequate to account for the behavior of IT bands.

It is reasonable to expect that arguments based on the dielectric continuum theory would give better agreement between theory and experiment if values for IT bands extrapolated to zero ionic strength were used instead of values measured without regard to the ionic environment present. We are further exploring these ideas, especially with regard to the possible differences in ionic strength on electron transfers proceeding by purely adiabatic mechanisms and those, such as that which occurs in complex I, in which a significant degree of tunnelling occurs.

Acknowledgment. We are grateful to the National Institutes of Health (Grant No. GM 36857) for generous support of this research.

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Three-Center Binding of a Nitroxyl Free Radical to Copper(II) Bromide

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Transition-metal–nitroxyl complexes are currently of great interest since they are now used in the design of new magnetic materials.[2,3] Copper(II)–nitroxyl species exhibit remarkable magnetic properties which are strongly correlated to their coordination geometry; complexes with an equatorially bound nitroxyl ligand[4-7] exhibit strong antiferromagnetism, while those containing

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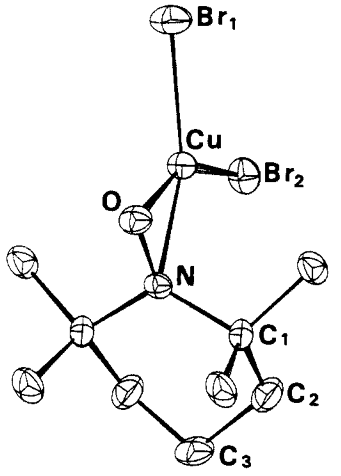

Figure 1. ORTEP view of $CuBr_2$·Tempo. Relevant bond lengths and angles are as follows: Cu–Br(av) = 2.270 (2), Cu–O = 1.860 (5), Cu–N = 1.998 (7), O–N = 1.304 (8) (Å); Br–Cu–Br = 106.5 (1), O–Cu–N = 39.3 (2) (deg).

an axial nitroxide exhibit a ferromagnetic behavior.[8-10] In both cases the free radical is bound to the copper ion through a metal–oxygen bond. We have now been able to prepare and characterize by X-ray diffraction methods the adduct of copper(II) bromide with 2,2,6,6-tetramethylpiperidinyl-1-oxy (Tempo). This adduct is the first metal–nitroxyl complex in which both the oxygen and nitrogen atoms are coordinated to the metal center; to our knowledge it also affords the first example of a three-membered metallacycle including copper.

The compound was prepared by mixing equimolar amounts of Tempo and copper(II) bromide–acetonitrile complex in diethyl ether. Recrystallization of the precipitate in a methylene chloride–diethyl ether mixture (1:1) afforded dark brown crystals indefinitely stable at room temperature in the absence of moisture.

The molecular structure[11] of the adduct was determined by X-ray diffraction techniques and is shown in Figure 1. The most striking feature of this structure is the binding of the Tempo fragment to the metal ion by both the O and N atoms at distances of Cu–O = 1.860 (5) Å and Cu–N = 1.998 (7) Å. The $CuBr_2$ moiety as well as the O, N, and C_3 atoms of Tempo are located in the symmetry plane of the molecule. Therefore the coordination geometry of the copper ion can be described approximately as square planar; however, the N–O bond length of 1.304 (8) Å leads to severe angular distortions from this idealized bonding pattern. The structural parameters of the nitroxyl fragment need some comments. The NO bond length is slightly longer than that found in Tempo itself, and the usual[13] pyramidal shape of the C_2NO group is, in $CuBr_2$·Tempo, much more pronounced than in uncomplexed nitroxides or in those which are bound to the metal ion only by the oxygen atom. This is understandable since since in $CuBr_2$·Tempo the nitrogen atom is also bound to the metal and like other four-coordinated nitrogens is expected to be tetrahedral. However, the structural features of the Tempo fragment, in $CuBr_2$·Tempo are significantly different from those of Tempo.

Variable-temperature (6–300 K) susceptibility data were collected at a magnetic field strength of 0.5 T. The adduct is essentially diamagnetic over the entire temperature range investigated. The effective magnetic moment varies only slightly from 0.02 to 0.15 μ_B over this temperature range. The increase in susceptibility at low temperature is consistent with a small amount of paramagnetic impurity (<1%), a common occurrence in Cu(II) complexes with singlet ground states.[4]

Copper complexes with nitroxides in which the free radical is equatorially bound to the metal only by the oxygen atom are also diamagnetic.[4-7] Since, in these compounds, the structural features of the Tempo fragment are identical with those of the uncomplexed nitroxide, they are commonly accepted as true copper(II)–free radical species. Unfortunately, the description of $CuBr_2$·Tempo is not so straightforward. Actually the same η^2 bonding to the metal and a similar pronounced pyramidal shape of the C_2NO group have been reported for the reduced form of Tempo in two platinum(II) complexes.[14] This raises the question as to whether the peculiarity of the structural parameters is the consequence of a copper-to-nitroxide electron transfer.

Redox processes have been shown to be operative in copper(II)–nitroxyl systems, but in all the known examples reported so far[15,16] the reverse electron transfer from the free radical to the metal, corresponding to an oxidation of the nitroxide, has been established. Preliminary studies of the solution properties of $CuBr_2$·Tempo show that the complex is not dissociated in methylene chloride;[17] however, dissociation occurred on silica gel resulting in a *quantitative yield* of Tempo. In addition, the reactivity of these solutions toward benzyl alcohol[18] is identical with that previously described for mixtures of copper(II) halides and Tempo.[15] Since it has been shown that, for these mixtures, the oxidizing intermediate was the nitrosonium ion, it is expected that in $CuBr_2$·Tempo any electron transfer would also correspond to the oxidation of the nitroxide. Additional support of this behavior comes from the energy level ordering of the complex as determined by Extended Huckel calculations.[19] It is seen that the SOMO's of the two fragments, $CuBr_2$ and Tempo, interact leading to two MO's separated by an energy gap of 1.2 ev. The MO of higher energy is made up of the nitroxyl π^* orbital and a small amount of the metal $d_{x^2-y^2}$ orbital, while the MO of lower energy has a predominantly copper $d_{x^2-y^2}$ component. Owing to the large energy gap, it is anticipated that the adduct will have a ground singlet state. Moreover, pairing of the two single electrons in the orbital of lower energy would lead to a HOMO with a pronounced copper $d_{x^2-y^2}$ character. Accordingly, the adduct would be described as a $Cu(I)–N^+{=}O$ complex. This description is strongly at variance with the structural parameters, since for a nitrosonium ion, a planar C_2NO fragment and a short N–O bond of 1.22 Å are expected.[16,20] It appears, therefore, that $CuBr_2$·Tempo cannot be described as a complex of the reduced form of Tempo nor as a complex of its oxidized form. Thus, we are led to infer that the apparent diamagnetism of the new compound is a consequence of the symmetry-allowed overlap of the two magnetic orbitals of $CuBr_2$ and Tempo, rather than an actual pairing of the two unpaired electrons.

In summary, we propose that the new adduct is best described as a strongly antiferromagnetically coupled copper(II)–nitroxyl species in which the particular shape of the Tempo fragment is probably due to its unusual η^2 coordination.

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Registry No. $CuBr_2$·Tempo, 113132-33-5; benzyl alcohol, 100-51-6; benzaldehyde, 100-52-7.

Supplementary Material Available: Listing of atomic positional parameters (1 page). Ordering information is given on any current masthead page.

The Electronic Structures of *trans*- and *cis*-Bicyclo[4.1.0]hept-3-ene. Evidence for a Twist, Bent σ Bond

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trans-Bicyclo[4.1.0]hept-3-ene (**1**) has been synthesized recently,[1] and its isomerization to its cis isomer **2**[2] has been studied.[3] Hydrocarbon **1** is of interest because of the possible presence of a twist, bent σ bond between the bridgehead carbons C_1 and C_6.[4]

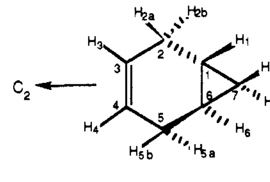

TOP VIEW


EDGE VIEW

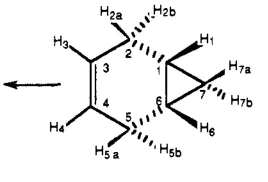
Although two decades have passed since the existence of this novel type of carbon–carbon bonding was first proposed,[4] unequivocal evidence for the presence of a twist–bent carbon–carbon σ bond has not been presented.[3] Herein, we present the results of our theoretical calculations on whether such novel bonding exists in **1** or **2**.

The ab initio calculations were done by using the program GRADSCF[5] on a CRAY-1A computer. Initial geometries were constructed by using CHEMX[6] and partially optimized. Subsequently, the geometries were symmetrized, **1** (C_2) and **2** (C_s), and gradient[7] optimized at the SCF level with the STO-3G basis set.[8] The final gradient optimizations were done with a double-ζ basis set augmented by d functions on carbon giving a basis set of the form (9s5p1d/4s)/[3s2p1d/2s].[9,10] At the optimimum SCF geometry, the force field was determined analytically[11] together with a correction for correlation effects at the MP2 level.[12]

Table I. Optimized Structural Parameters for **1** and **2**



1



2

	Bond Distances (Å)		
$r(C_1–C_7)$	1.509	$r(C_1–C_7)$	1.503
$r(C_1–C_6)$	1.491	$r(C_1–C_6)$	1.506
$r(C_1–C_2)$	1.511	$r(C_1–C_2)$	1.519
$r(C_2–C_3)$	1.541	$r(C_2–C_3)$	1.508
$r(C_3–C_4)$	1.340	$r(C_3–C_4)$	1.325
$r(C_1–H_1)$	1.080	$r(C_1–H_1)$	1.077
$r(C_2–H_{2a})$	1.087	$r(C_2–H_{2a})$	1.087
$r(C_2–H_{2b})$	1.086	$r(C_2–H_{2b})$	1.087
$r(C_3–H_3)$	1.078	$r(C_3–H_3)$	1.078
$r(C_7–H_7)$	1.077	$r(C_7–H_{7a})$	1.078
		$r(C_7–C_{7b})$	1.077
	Bond Angles (deg)		
$\theta(C_1–C_7–C_6)$	59.2	$\theta(C_1–C_7–C_6)$	60.1
$\theta(C_1–C_7–H_{7a})$	115.1	$\theta(C_1–C_7–H_{7a})$	117.5
$\theta(C_1–C_7–H_{7b})$	121.9	$\theta(C_1–C_7–H_{7b})$	118.3
$\theta(H_{7a}–C_7–H_{7b})$	113.6	$\theta(H_{7a}–C_7–H_{7b})$	114.6
$\theta(C_6–C_1–C_7)$	60.4	$\theta(C_6–C_1–C_7)$	59.9
$\theta(C_2–C_1–C_7)$	141.3	$\theta(C_2–C_1–C_7)$	120.0
$\theta(C_2–C_1–C_6)$	109.4	$\theta(C_2–C_1–C_6)$	120.6
$\theta(C_7–C_1–H_1)$	109.0	$\theta(C_7–C_1–H_1)$	115.7
$\theta(C_6–C_1–H_1)$	111.1	$\theta(C_6–C_1–H_1)$	116.0
$\theta(C_2–C_1–H_1)$	109.3	$\theta(C_2–C_1–H_1)$	114.1
$\theta(C_1–C_2–C_3)$	102.2	$\theta(C_1–C_2–C_3)$	113.9
$\theta(C_1–C_2–H_{2a})$	113.9	$\theta(C_1–C_2–H_{2a})$	109.3
$\theta(C_1–C_2–H_{2b})$	113.3	$\theta(C_1–C_2–H_{2b})$	109.8
$\theta(C_3–C_2–H_{2a})$	109.8	$\theta(C_3–C_2–H_{2a})$	108.3
$\theta(C_3–C_2–H_{2b})$	110.6	$\theta(C_3–C_2–H_{2b})$	109.1
$\theta(H_{2a}–C_2–H_{2b})$	107.1	$\theta(H_{2a}–C_2–H_{2b})$	106.1
$\theta(C_2–C_3–C_4)$	125.3	$\theta(C_2–C_3–C_4)$	125.0
$\theta(C_2–C_3–H_3)$	116.7	$\theta(C_2–C_3–H_3)$	116.2
$\theta(C_3–C_4–H_4)$	117.9	$\theta(C_3–C_4–H_4)$	118.8

The optimized geometries are given in Table I. The cis isomer **2** should not have significantly more strain than that associated with cyclopropane, and the structural parameters should be those for normal hydrocarbons. In support of this premise, the C–C bonds in the cyclopropane moiety of **2** are essentially the same as those found for cyclopropane with this basis set.[13] The only change is in $\theta(C_2C_1C_7)$ which is increased by 2°. The double bond of **2** also has the expected geometry parameters.[10] Overall the only significant differences from a "normal" bonding parameter for **2** occurred at C_2 where $\theta(C_1C_2C_3)$ increased by 4.4° from the tetrahedral value and $\theta(H_{2a}C_2H_{2b})$ was 3.4° smaller than tetrahedral.

Our calculations for the trans isomer **1** show significant deviations in the bond angle parameters relative to **2**. In comparison, only modest changes are found for the bond lengths. For example, $r(C_3{=}C_4)$ increased by 0.015 Å and $r(C_2–C_3)$ increased by 0.033 Å in **1** relative to **2**. This change in $r(C_2–C_3)$ gave a bond length significantly longer than a normal sp^2–sp^3 bond. The bond lengths

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