wherein aromatic amines are thought to quench π-π^* singlets by charge-transfer interactions. It appears that attack at an electron of nitrogen occurs for π-π^* triplet states and perhaps for n-π^* triplet states as well, although rapid γ-hydrogen abstraction by the n-π^* state is not necessarily eliminated from the available data. The above scheme would predict a decrease in the quantum efficiency of reaction as the pair of electrons on nitrogen become less available. Preliminary experiments have shown that the quantum yield of the photoreaction decreases substantially when the substituted phenacylamine (I and/or II) is converted to its "onium" derivative by protonation.

Electron-transfer processes also seem to be important in the photochemistry of aroylaziridines and -azetidines[24] and in fact may be a general phenomenon in the photochemistry of many nitrogen-containing compounds. Further work both on the mechanism of the rearrangement and on the scope and application to other heteroatoms is currently under way and will be the subject of future reports.

Acknowledgment. The authors are indebted to the National Science Foundation (Grant GP-9385) for generous support of this research.

[24] R. Gruber and W. Eisenhardt unpublished results. See A. Padwa and R. Gruber, *J. Am. Chem. Soc.*, **90**, 4456 (1968); A. Padwa and W. Eisenhardt, *ibid.*, **90**, 2442 (1968).

[25] Alfred P. Sloan Fellow, 1968–1970.

Albert Padwa,[25] William Eisenhardt
Robert Gruber, Deran Pashayan
Department of Chemistry, State University of New York at Buffalo, Buffalo, New York 14214

Received October 14, 1968

Jahn–Teller Distortions in Octahedral Copper(II) Complexes

Sir:

Recently, there has been an interest in the existence (or nonexistence) of Jahn–Teller distortions in the tris chelates of copper(II)[1] and manganese(III).[2] We wish to report our X-ray diffraction and electron spin resonance studies of the novel bipyridine (bipy) adduct of bis(hexafluoroacetylacetonato)copper(II), Cu(hfacac)$_2$. This unusual molecule distorts two of the three symmetrical chelating ligands to remove the orbital degeneracy present in an octahedral d^9 configuration. Therefore, the present study provides the first example of a symmetrical ligand undergoing distortion because of the Jahn–Teller effect in the copper(II) ion.

A series of similar complexes is easily prepared by treating either bis(hexafluoroacetylacetonato)copper(II) or bis(theonyltrifluoroacetonato)copper(II) with either bipyridine or 1,10-phenanthroline. For example, if solutions of Cu(hfacac)$_2$ and bipy in a minimum amount of chloroform are mixed, a green precipitate is formed.

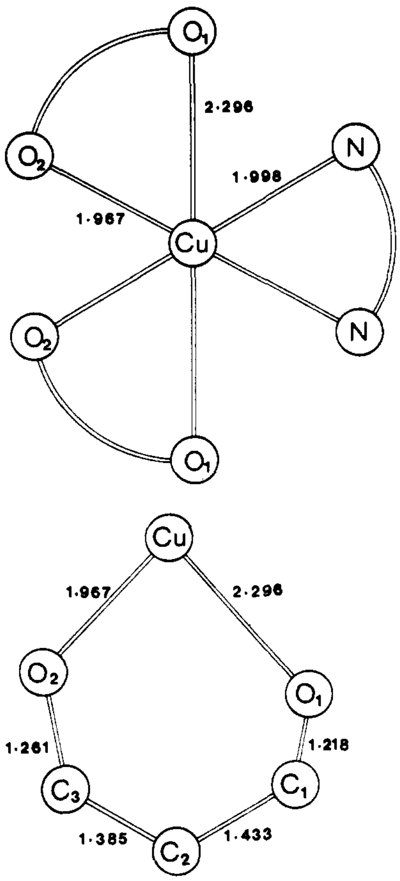


Figure 1. The upper figure gives the over-all geometry of the Cu(hfacac)$_2$·bipy adduct together with the Cu–O and Cu–N bond lengths. The twofold axis bisects the bipy ligand represented by N–N. The hfacac ligand is represented by O–O. The lower figure gives the bond distances in the β-diketone–Cu ring system and shows the alternation of bond lengths resulting from the Jahn–Teller distortion.

The complex can be recrystallized from benzene in the form of long, bright green needles. The analysis corresponds to the 1:1 complex. *Anal.* Calcd for $F_{12}C_{10}O_4H_2Cu \cdot C_{10}N_2H_8$: C, 37.88, H, 1.88; N, 4.42. Found: C, 37.69; H, 1.44; N, 4.44.

Single-crystal X-ray studies revealed that the crystals are monoclinic with $a = 16.55$, $b = 16.62$, $c = 8.80$ Å and $\beta = 100.7°$. The space group is either Cc or C2/c, with the latter preferred on the basis of intensity statistics. With four molecules per unit cell (the densities are 1.740 g/cm^3 observed and 1.755 g/cm^3 calculated), the molecule is required to have a twofold symmetry axis. The intensity data were measured by the stationary crystal–stationary counter method using an automatic diffractometer. A total of 6688 measurements were made and reduced to a unique set of 2036 reflections of which 1768 were considered observed and used in the analysis. The structure was solved by locating the copper atom in the Patterson function and locating the light atoms by using a minimum function and Fourier syntheses. The trial structure was refined by isotropic least squares to an R (the usual residual) of 18.7% and by anisotropic least squares to an R of 8.0%. The location of the hydrogen atoms and further refinement are continuing.

The molecule is illustrated in Figure 1 together with some pertinent bond distances. The twofold axis passes through the bipy ligand and requires the two Cu–N bonds

[1] M. D. Joesten, M. S. Hussain, P. G. Lenhert, and J. H. Venable, Jr., *J. Am. Chem. Soc.*, **90**, 5623 (1968).

[2] T. S. Davis, J. P. Fackler, and M. J. Weeks, *Inorg. Chem.*, **7**, 1994 (1968).

to be identical. The two Cu–O bonds in the plane defined by the Cu and N atoms are slightly shorter than the Cu–N bonds, as is usually the case. Both the Cu–O bond length of 1.967 ± 0.004 Å and the Cu–N bond length of 1.998 ± 0.004 Å are similar to the distances found in other complexes with both nitrogen and oxygen atoms coordinated to the copper atom.[3] However, the Cu–O bonds to the second oxygen of each β-diketone ring are much longer, 2.296 ± 0.004 Å. Therefore, the four short–two long bond distortion of an octahedron is also found in this molecule. The bond lengths in the β-diketone moiety are given in Figure 1 and follow a pattern of alternating long and short bonds. The alternation of the bond lengths can easily be rationalized by the stronger interaction of one oxygen atom to the copper(II) ion.

Electron spin resonance studies were carried out on diluted solid samples of $Cu(hfacac)_2 \cdot bipy$ in $Zn(hfacac)_2 \cdot bipy$ which were prepared by cocrystallization of the two compounds from benzene. The optimum compromise between resolution and signal-to-noise ratio was found for a zinc:copper ratio in the solution of 50:1 although the final ratio in the solid was not determined.

The spectra of the diluted solid were recorded for both a finely powdered sample and a single crystal at several arbitrary orientations. Hyperfine interaction with one copper and two equivalent nitrogen nuclei was observed at each of the orientations of the single crystal. The spectrum of the powder at −150° was indicative of axial symmetry (about the O–Cu–O axis) at the copper atom. Observed parameters are $g_\parallel = 2.299 \pm 0.004$, $g_\perp = 2.056 \pm 0.004$; for Cu^{63} $A_\parallel = 151 \pm 2$ G; and for Cu^{65} $A_\parallel = 163 \pm 2$ G, $A_\perp = 26.6 \pm 1$ G. The difference between the isotopes of copper was not resolvable for the perpendicular features. The hyperfine splitting from two equivalent nitrogen nuclei was resolved on both the parallel ($A_N = 9.5 \pm 1$ G) and perpendicular ($A_N = 13.3 \pm 1$ G) features.

The measured g and A_{Cu} values are in accord with the values expected for a copper ion in a tetragonally distorted octahedral environment. However, whether the field is truly tetragonal or has some rhombic character could not be decided on the basis of the spectra obtained from the powdered sample. The anisotropy detected in the hyperfine splitting of the nitrogen nuclei deserves comment. Similar splittings have been observed for square-planar complexes,[4,5] although in each case these splittings were isotropic, and for a tetrahedral copper(II) complex,[6] where the splittings were also anisotropic. More extensive single-crystal studies are in progress to locate the principal direction of the nitrogen hyperfine tensor.

Acknowledgment. We wish to thank the National Research Council of Canada for support of this research.

---

(3) G. E. Gurr, *Acta Cryst.*, **B24**, 1511 (1968), and references therein.

(4) H. R. Gersmann and J. D. Swalen, *J. Chem. Phys.*, **36**, 3221 (1962).

(5) A. H. Maki and B. R. McGarvey, *ibid.*, **29**, 35 (1958).

(6) G. F. Kokoszka, C. W. Reiman, and H. C. Allen, Jr., *J. Phys. Chem.*, **71**, 121 (1967).

(7) Address all correspondence to this author.

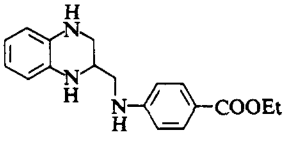
M. V. Veidis, G. H. Schreiber
T. E. Gough, Gus J. Palenik[7]
Department of Chemistry, University of Waterloo
Waterloo, Ontario, Canada

Received December 26, 1968

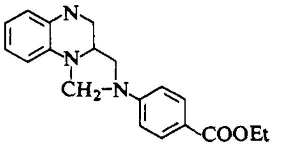
Kinetic Detection of the Imminium Cation in Formaldehyde–Amine Condensations in Neutral Aqueous Solution

Sir:

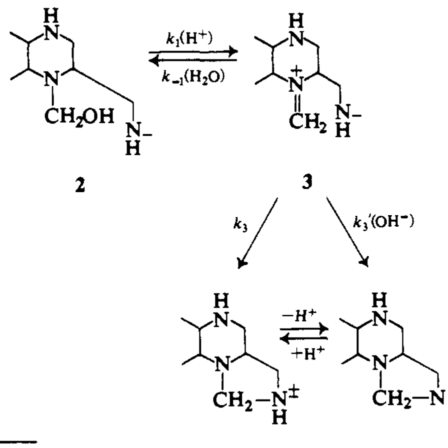
The intermediacy of the imminium cation in the Mannich condensations has been proposed by several investigators,[1-3] although its presence has never been unequivocally established except in strong acid solutions.[4] In our studies on the mechanism of action of tetrahydrofolic acid we have synthesized the model tetrahydroquinoxaline derivative **1** and investigated its condensation with formaldehyde to give **4**.[5] The pH–rate profile for the conversion of **1** to **4** in 50% v/v dioxane–water (μ = 0.2, 25°) monitored by the increase in absorption at 310 mμ is exhibited in Figure 1. The first-order rate constants, k_{obsd} (reproducible within ±5%), are obtained at kinetically saturating formaldehyde concentrations extrapolated to zero buffer concentration over the entire pH range studied; thus we conclude that **1** is in equilibrium with its respective carbinolamine **2**. The unique features of the pH–rate profile apparently arise from the conversion of carbinolamine to product. Although numerous investigations[6] have demonstrated that dehydration of **2** proceeds almost entirely through hydronium ion catalysis (Brønsted α = 0.7–0.9),[6] this profile does not follow first-order acid-catalyzed dehydration. The kinetic results may only be explained in terms of a steady-state species, logically the imminium cation **3**, whose partitioning is subject to pH control. Two mechanisms are proposed which yield the requisite expression for k_{obsd}, I (below) or II (not illustrated), which neglects $k_3'(OH^-)$ but



1



4



---

(1) H. Hellmann and G. Opitz, *Angew. Chem.*, **68**, 265 (1959).

(2) S. V. Liebermann and E. C. Wagner, *J. Org. Chem.*, **14**, 1001 (1949).

(3) (a) T. F. Cummings and J. R. Shelton, *ibid.*, **25**, 419 (1960); (b) R. G. Kallen and W. P. Jencks, *J. Biol. Chem.*, **24**, 5851 (1966).

(4) J. DeLuis, Ph.D. Thesis, The Pennsylvania State University, 1964.

(5) All compounds reported gave satisfactory elemental analyses and their structures were consistent with the infrared, mass, nmr, and ultraviolet spectral data.

(6) K. Koehler, W. Sandstrom, and E. H. Cordes, *J. Am. Chem. Soc.*, **86**, 2413 (1964), and references therein.