192 *Inorg. Chem.* **1980**, *19*, 192–195

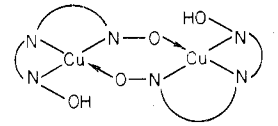
Contribution from the Department of Chemistry,
West Virginia University, Morgantown, West Virginia 26506

# Copper(II) Complexes Derived from 2,6-Diacetylpyridine Dioxime

G. A. NICHOLSON, C. R. LAZARUS, and B. J. McCORMICK*

*Received July 6, 1979*

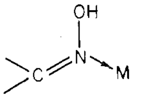
Complexes of copper(II) with the tridentate oxime ligand 2,6-diacetylpyridine dioxime (DAPDH$_2$) have been synthesized. The monomeric, five-coordinate complex Cu(DAPDH$_2$)Cl$_2$ forms readily from the ligand and CuCl$_2$·2H$_2$O. This complex is remarkably acidic, the p$K$ for proton dissociation being 2.8 ± 0.1 in water at 25.1 °C. The second proton is not removed by aqueous base. Deprotonation of Cu(DAPDH$_2$)X$_2$ in alcoholic solution leads to the dimeric dication [Cu(DAPDH)]$_2^{2+}$, which has been isolated as the chloride or tetrafluoroborate. In the dimer the fourth coordination position is occupied by an —O$^-$ donor derived from a deprotonated =N—O—H group to give a bridged chromophore of the type



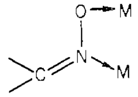
The copper centers are highly coupled, as indicated by the observed magnetic moment of 0.6 $\mu_B$/Cu$^{2+}$ and by the ESR spectrum. The dimeric structure is readily ruptured by coordinating solvents.

## Introduction

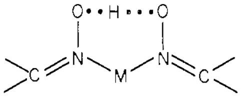
Although oximes are widely recognized as versatile ligands that form a variety of complexes, much remains to be learned about the types of structures that are formed as well as the factors that dictate structure. In general, the oxime function is known[1] to coordinate in four ways:



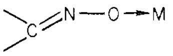
I



II



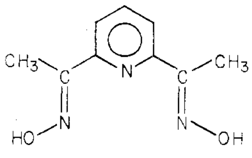
III



IV

Coordination modes I and III are observed most frequently, although it should be noted that the oxime function is a poor donor unless it is part of a chelate ring.

A particularly interesting chelating oxime is 2,6-diacetylpyridine dioxime, V, which will be abbreviated DAPDH$_2$.



V

This ligand was investigated by Hanania and co-workers,[2] who studied complexes of iron(II) in solution. It was found that p$K_a$ for the ligand dropped markedly upon coordination, an effect that was attributed to resonance stabilization of the anionic conjugate base. The only other work with DAPDH$_2$ as a ligand involves nickel. Following Hartkamp's report[3] that aqueous nickel(II) solutions of DAPDH$_2$ are oxidized by air, Baucom and Drago[4] isolated several complexes, including [Ni(DAPDH$_2$)$_2$]$^{2+}$, the deprotonated species [Ni(DAPD)$_2$]$^{2-}$, and the formally Ni(IV) complex Ni(DAPD)$_2$. Subsequently Sproul and Stucky[5] reported the crystal structure of Ni(DAPD)$_2$ and showed that the ligand is planar with coordination through nitrogen and that considerable strain is introduced into the DAPD$^{2-}$ moiety when it coordinates to nickel.

In view of the potentially interesting acid–base chemistry of coordinated DAPDH$_2$ and its apparent ability to stabilize high oxidation states by virtue of its strong $\sigma$-donor capability, we have extended the previous studies to several other metals. Reported here are the results of some of our work with copper.

## Experimental Section

**Materials and Analyses.** Routine chemicals were of reagent grade and were used without further purification. C, H, and N analyses were performed by Galbraith Microanalytical Laboratories. Chloride was determined gravimetrically as AgCl. Aldrich Chemical Co. supplied the 2,6-diacetylpyridine.

**Instrumentation.** Electronic spectra were measured at room temperature with a Cary Model 14 spectrophotometer. Infrared spectra were measured with a Beckman IR-12 spectrophotometer, and all samples were mulled with Nujol. Conductivities were measured at 25 ± 1 °C by using a Serfass conductivity bridge, YSI 3403 conductivity cell, and solvents that were purified by standard techniques.[6] The hydrogen ion concentration in the potentiometric titrations was determined with a Corning Digital 112 Research Model pH meter. All titrations were carried out in a double-walled cell of 50 mL capacity, and the temperature of all solutions was maintained at 25.1 ± 0.2 °C by circulation of thermostated water through the outer jacket of the cell. The ionic strength was maintained at 0.10 M with KNO$_3$, and all titrations were carried out under N$_2$. The ESR spectra were obtained with a Varian E-3 or E-109 spectrometer. Powder spectra and frozen solution spectra (liquid N$_2$) were obtained by using a standard quartz cell. Solution spectra were run in a special quartz cell designed for use with high-dielectric solvents. Room-temperature magnetic moments were measured with a Faraday balance of standard design. The calibrant was [Ni(en)$_3$](S$_2$O$_3$).[7]

Pascal's constants[8] were used to estimate the diamagnetic susceptibility of DAPDH$_2$, Cu$^{2+}$, Cl$^-$, and BF$_4^-$. The values used were 88.7 × 10$^{-6}$, 12.8 × 10$^{-6}$, 23.4 × 10$^{-6}$, and 38.2 × 10$^{-6}$, respectively.

**Synthesis of DAPDH$_2$.** The ligand was prepared in a manner similar to that reported by Baucom and Drago.[4] A solution of 4.70 g (67.5 mmol) of NH$_2$OH·HCl and 2.70 g (67.5 mmol) of NaOH in 40 mL of 50% aqueous methanol was added to a boiling solution of 5.00 g (30.6 mmol) of 2,6-diacetylpyridine in 150 mL of methanol. The resulting mixture was refluxed for 2 h, cooled, and diluted with 150 mL of water. The mixture was then filtered, and the white solid isolated was washed thoroughly with water and recrystallized from methanol.

**Synthesis of [Cu(DAPDH$_2$)Cl$_2$].** To a solution of 0.432 g (2.53 mmol) of CuCl$_2$·2H$_2$O in 25 mL of methanol was added 0.500 g (2.58

---

(1) Chakravorty, A. *Coord. Chem. Rev.* **1974**, *13*, 1.
(2) Hanania, G. I. H.; Irvine, D. H.; Shurayh, F. *J. Chem. Soc.* **1965**, 1149.
(3) Hartkamp, H. *Fresenius' Z. Anal. Chem.* **1960**, *178*, 19.
(4) Baucom, E. I.; Drago, R. S. *J. Am. Chem. Soc.* **1971**, *93*, 6469.
(5) Sproul, G.; Stucky, G. D. *Inorg. Chem.* **1973**, *12*, 2898.
(6) Geary, W. J. *Coord. Chem. Rev.* **1971**, *7*, 81.
(7) Earnshaw, A. "Introduction to Magnetochemistry"; Academic Press: New York, 1968.
(8) Figgis, B. N.; Lewis, J. "Modern Coordination Chemistry"; Lewis, J., Wilkins, R. G., Eds.; Interscience Publishers: New York, 1960.

0020-1669/80/1319-0192$01.00/0 © 1980 American Chemical Society

Table I. Conductivity Data: $\Lambda_M$[a]

| | nitromethane | 1/3 methanol–nitromethane |
|---|---|---|
| $Cu(DAPDH_2)Cl_2$[b] | 5.0 | |
| $[Cu(DAPDH)]_2Cl_2$[b] | | 138 |
| $[Cu(DAPDH)]_2(BF_4)_2$[b] | 90.1 | 112 |

[a] $\Omega^{-1}$ cm$^2$ mol$^{-1}$. [b] $10^{-3}$ M.

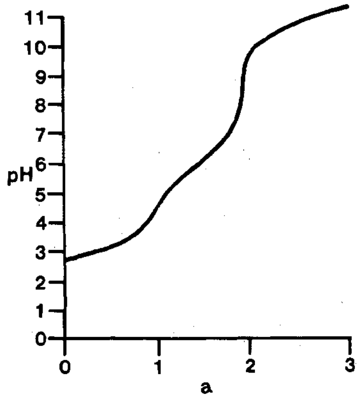


**Figure 1.** Titration curve of $Cu(DAPDH_2)Cl_2$ with 0.0925 M NaOH in water (*a* is moles of base per mole of $Cu(DAPDH_2)Cl_2$).

mmol) of $DAPDH_2$. The mixture was stirred for 10 min, and then the volume of the resulting solution was reduced to 10 mL by evaporation in a stream of $N_2$ gas, yielding green crystals. The mixture was then treated with 10 mL of anhydrous ether and cooled, providing more green crystals. The green solid so obtained was washed with three 40-mL portions of anhydrous ether and recrystallized from methanol. Anal. Calcd for $C_9H_{11}Cl_2CuN_3O_2$: C, 32.99; H, 3.38; N, 12.82; Cl, 21.4. Found: C, 32.76; H, 3.41; N, 12.60; Cl, 21.1.

**Synthesis of $[Cu(DAPDH)]_2Cl_2$.** A mixture of 0.515 g (1.57 mmol) of $[Cu(DAPDH_2)Cl_2]$ and 0.90 g (2.25 mmol) of NaOH in 50 mL of 50/50 methanol-2-propanol was stirred for 20 min. The mixture was filtered, and the volume of the filtrate was reduced to 20 mL in a $N_2$ gas stream. Anhydrous ether was then slowly added until the solid precipitated from the solution. The dark green solid so obtained was washed with three 40-mL portions of anhydrous ether and recrystallized from methanol. Anal. Calcd for $C_{18}H_{20}Cl_2Cu_2N_6O_4$: C, 37.12; H, 3.46; N, 14.42. Found: C, 37.25; H, 3.60; N, 14.26.

**Synthesis of $[Cu(DAPDH)]_2(BF_4)_2$.** A mixture of 1.40 g (6.33 mmol) of $CuCO_3 \cdot Cu(OH)_2$ and 1.40 g of 50% $HBF_4$ in 30 mL of absolute ethanol was stirred for 20 min. The mixture was filtered, and to the light blue filtrate was added with stirring 0.524 g (2.70 mmol) of $DAPDH_2$. After 15 min, a greenish black precipitate settled to the bottom of the container. The precipitate was isolated by filtration and washed with three 40-mL portions of anhydrous ether. The product was then recrystallized from methanol by the addition of ether and then again washed with three 40-mL portions of anhydrous ether. Anal. Calcd for $C_{18}H_{20}B_2F_8Cu_2N_6O_4$: C, 31.48; H, 2.91; N, 12.24. Found: C, 31.58; H, 3.00; N, 12.22.

## Results

Copper(II) chloride reacts with $DAPDH_2$ in methanol to give the green compound $Cu(DAPDH_2)Cl_2$, a complex that is quite soluble in polar hydrogen-bonding solvents but is of low solubility in other solvents. In nitromethane the complex is a nonconductor (Table I) indicating that both chloride ions are coordinated. The room-temperature magnetic moment is 1.90 $\mu_B$. Aqueous solutions of $Cu(DAPDH_2)Cl_2$ are quite acidic and can be titrated with base, as shown in Figure 1. Initially it was thought that the two inflections in the titration curve represented reactions 1 and 2, respectively, and attempts were made to calculate corresponding $pK_1$ and $pK_2$ values. Constant $pK_1$ values were obtained from data points between the first 10% and the last 10% of the buffer zone preceding the first inflection point. The value of 2.8 ± 0.1 for $pK_1$ at 25.1 °C appears to be consistent with reaction 1 and the observed acidity of aqueous solutions of $Cu(DAPDH_2)Cl_2$. Similar attempts to calculate a $pK_2$ value from data points in the second buffer region were not successful, as the value obtained increased steadily with moles of base. This indicates that the second inflection point is *not* attributable solely to reaction 2. Some other base-consuming reaction must be involved. The second reaction could conceivably involve the substitution of $OH^-$ for $Cl^-$ in the coordination sphere, but direct evidence for the existence of hydroxo complexes was not obtained.

$$Cu(DAPDH_2)Cl_2 + OH^- \rightarrow Cu(DAPDH)Cl_2^- + H_2O \qquad (1)$$

$$Cu(DAPDH)Cl_2^- + OH^- \rightarrow Cu(DAPD)Cl_2^{2-} + H_2O \qquad (2)$$

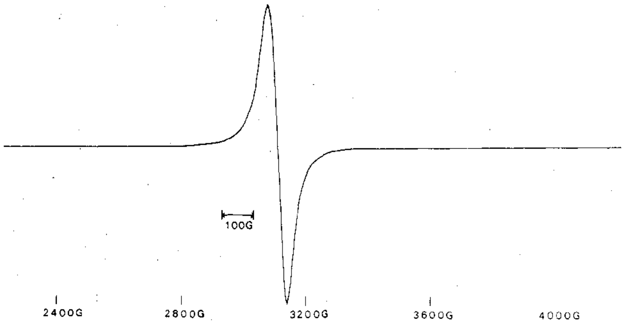


**Figure 2.** ESR spectrum of $Cu(DAPDH_2)Cl_2$ in methanol.

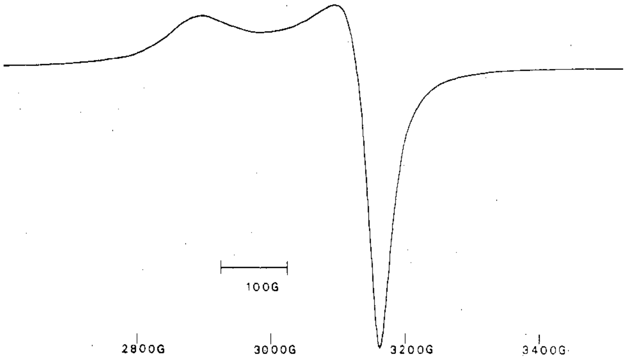


**Figure 3.** Powder ESR spectrum of $Cu(DAPDH_2)Cl_2$.

The electronic absorption spectrum of $Cu(DAPDH_2)Cl_2$ in methanol exhibits a broad band centered at 736 nm, with $\epsilon$ = 95.4 L cm$^{-1}$ mol$^{-1}$. Upon treatment of $Cu(DAPDH_2)Cl_2$ solutions with base and concomitant deprotonation of the oxime ligand, the maximum shifts to shorter wavelengths, corresponding to an increase in *Dq*. This observation is consistent either with the substitution of a stronger ligand for $Cl^-$ in the coordination sphere (probably with dimer formation, vide infra) or with deprotonation of the ligand, as Baucom and Drago[4] found *Dq* values of 1214 cm$^{-1}$ and 1580 cm$^{-1}$ for respective nickel complexes of $DAPDH_2$ and $DAPD^{2-}$.

The ESR spectrum of $Cu(DAPDH_2)Cl_2$ in methanol is shown in Figure 2. Single-line ESR spectra for solutions containing copper(II) are not common, but other examples are known.[9] The ESR spectrum of powdered $Cu(DAPDH_2)Cl_2$ at 78 K is shown in Figure 3. The spectrum is consistent with axial symmetry for the complex.

Isolation of a singly deprotonated complex was accomplished by treating $Cu(DAPDH_2)Cl_2$ with base in alcoholic solvent. For comparison purposes a similar complex containing the noncoordinating anion $BF_4^-$ was prepared from $Cu(BF_4)_2$

---

[9] Wasson, J. R. *Spectrosc. Lett.* **1976**, *9*, 95.

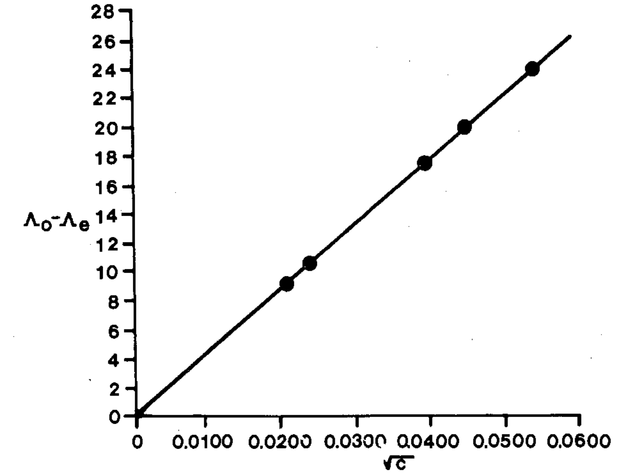


**Figure 4.** Onsager plot of conductivity data for $[Cu(DAPDH)]_2(BF_4)_2$.

Table II. Spectral Data

| | $\lambda_{max}$, nm | $\epsilon$, L cm$^{-1}$ (mol of Cu)$^{-1}$ | $\nu_{C=N}$, cm$^{-1}$ |
|---|---|---|---|
| $Cu(DAPDH_2)Cl_2$ | 736 | 95.4 | 1589 |
| $[Cu(DAPDH)]_2Cl_2$ | 610 | 198 | 1590, 1515 |
| $[Cu(DAPDH)]_2(BF_4)_2$ | 610 | 184 | 1600, 1530 |

according to reaction 3. Both the chloride and the tetrafluoroborate complex were soluble in water and methanol.

$$2Cu(BF_4)_2 + 2DAPDH_2 \rightarrow [Cu(DAPDH)]_2(BF_4)_2 + 2HBF_4 \quad (3)$$

The complexes formed upon monodeprotonation of the ligand were studied in solution by detailed conductivity measurements. The $BF_4^-$ salt was sufficiently soluble for study in pure nitromethane, but the $Cl^-$ salt did not provide sufficient concentrations in pure nitromethane; hence, the chloride was characterized in the mixed solvent. For comparison purposes the $BF_4^-$ salt also was characterized in the mixed solvent. The conductivity results are given in Table I, and an Onsager plot ($\Lambda_0 - \Lambda_e$ vs. $c^{1/2}$) of the data obtained in nitromethane solvent is given in Figure 4, where the slope of the line is 400. As discussed by Feltham and Hayter,[10] a slope of this magnitude clearly establishes the electrolyte type as 2:1; hence, the tetrafluoroborate is confirmed as a dimer having the formula $\{[Cu(DAPDH)]_2\}(BF_4)_2$ in nitromethane solvent. The dimeric structure is retained in the solid state, as shown by an X-ray crystallographic study.[11] Owing to the similar conductivity properties exhibited by the $BF_4^-$ and the $Cl^-$ salts, the latter is also considered to contain a dimeric cation in the solid state and in noncoordinating solvents.

Solutions of $[Cu(DAPDH)]_2Cl_2$ are neutral in an aqueous medium, whereas $[Cu(DAPDH)]_2(BF_4)_2$ is acidic. The observed acidity in the latter case probably is due to the hydrolysis of $BF_4^-$ instead of additional proton dissociation from the ligand.

Electronic spectral data are given in Table II, where it can be seen that the two dimers provide identical spectra. The magnetic moment of $[Cu(DAPDH)]_2(BF_4)_2$ is 0.6 $\mu_B$/Cu at 25 °C.

A room-temperature ESR spectrum of a powdered sample of $[Cu(DAPDH)]_2(BF_4)_2$ is shown in Figure 5. The spectrum is typical of that shown by other highly coupled copper(II) dimers.[12] The spectral lines delineated by the rectangular box in Figure 5 are attributable to a low concentration (estimated to be 2% from line intensities) of a copper(II) monomer of unknown composition cocrystallized with the sample. The monomer apparently arises during either recrystallization or grinding of the dimer. When dissolved in coordinating solvents such as *N,N*-dimethylformamide, the sample provided a four-line spectrum typical of monomeric copper(II) species.

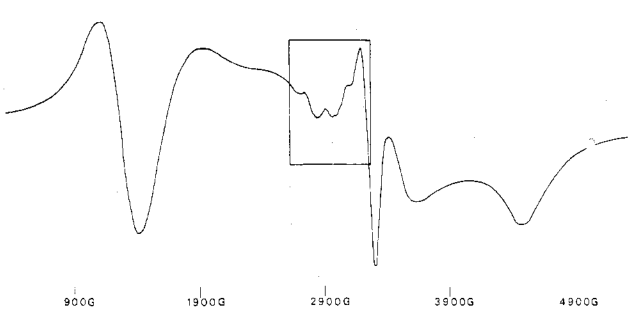


**Figure 5.** Powder ESR spectrum of $[Cu(DAPDH)]_2(BF_4)_2$ at 25 °C.

Infrared spectra of all of the complexes show characteristic oxime features that generally do not require comment. Major bands attributable to C=N stretching motions are observed in the 1500–1600 cm$^{-1}$ range (Table II). A new band appears at ca. 1520 cm$^{-1}$ in the spectra of the deprotonated complexes.

## Discussion

The crystal structure[5] of $Ni(DAPD)_2$ reveals that the tridentate doubly deprotonated ligand is planar and that it coordinates through the pyridine and oxime nitrogen atoms. Although crystallographic evidence relating to the protonated form of the ligand is unavailable, it is reasonable to assume that in this form also the oxime nitrogen atoms coordinate instead of the oxygen atoms. This assumption is consistent with the preferred mode of coordination for oximes.[1] Since $Cu(DAPDH_2)Cl_2$ is a nonelectrolyte, the chlorides must be coordinated to give a five-coordinate structure. A few similar complexes are known. The complex formed from copper(II) chloride and 2,2′,2″-terpyridine[13] is five-coordinate, with a distorted trigonal-bipyramidal structure, and 2,6-di-2′-quinolylpyridine (dqp), which should be similar to $DAPDH_2$, gives five-coordinate complexes of the type $Cu(dqp)Cl_2$.[14] A $C_{2v}$ structure was assigned[14] to the latter complex on the basis of the powder EPR spectrum, in which the *g* anisotropy was completely resolved. In solutions at room temperature, only one line was observed, as is the case for $Cu(DAPDH_2)Cl_2$. It is reasonable to assume that $Cu(dqp)Cl_2$ and $Cu(DAPDH_2)Cl_2$ have similar structures. The bulk magnetic moment of $Cu(DAPDH_2)Cl_2$ is similar to that observed for a large number of other copper(II) complexes in a variety of coordination geometries.

The acidity of $Cu(DAPDH_2)Cl_2$ is remarkable, there being a decrease of approximately 7.2 units in the p$K_1$ of the ligand upon coordination to copper. The previously studied iron(II) complexes also have reduced p$K$ values.[2] The magnitude of p$K_1$ and p$K_2$ for $Fe(DAPDH_2)_2^{2+}$ was not determined; however, p$K_3$ and p$K_4$ were estimated to be ~5 and ~7, respectively. Unfortunately no direct comparison of the effect of $Cu^{2+}$ and $Fe^{2+}$ on the acidity of $DAPDH_2$ can be made since equilibrium data on comparable ionization reactions are unavailable, but one would expect the acidity enhancement to be greater in the copper(II) case, since iron(II) is larger and less polarizing. This trend has been observed in other systems.[15] Enhanced acidity in the copper(II) system cannot

---

(10) Feltham, R. D.; Hayter, R. G. *J. Chem. Soc.* **1964**, 4587.

(11) Nicholson, G. A.; Petersen, J. L.; McCormick, B. J. *Inorg. Chem.*, following paper in this issue.

(12) Wasson, J. R.; Shyr, C.-I.; Trapp, C. *Inorg. Chem.* **1968**, *7*, 469.

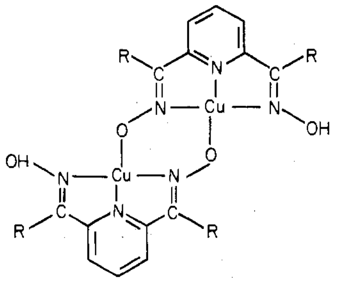
(13) Harris, C. M.; Lockyer, T. N.; Stephenson, N. C. *Aust. J. Chem.* **1966**, *19*, 1741.

(14) Wasson, J. R.; Klassen, D. M.; Richardson, H. W.; Hatfield, W. E. *Inorg. Chem.* **1977**, *16*, 1906.

(15) Smith, R. M.; Martell, A. E. "Critical Stability Constants"; Plenum Press: New York, 1976; Vol. 4.

be attributed to dimer formation since, as will be discussed below, the dimers are easily ruptured by coordinating solvents. In addition, it should be emphasized that there was no evidence for dimer formation in the aqueous titration studies.

The complex cationic dimer that is formed upon deprotonation of $Cu(DAPDH_2)Cl_2$ in nonaqueous solvents of low-coordinating ability has the structure[11]



The dimeric structure is retained in noncoordinating solvents, but in coordinating solvents the dimer dissociates with concomitant entry of solvent molecules into the copper coordination sphere. This is evidenced by the fact that a four-line ESR spectrum typical of monomeric copper complexes is exhibited by such solutions.

In the dimer the copper(II) centers clearly are highly coupled magnetically,[16] as evidenced by the room-temperature moment of 0.6 $\mu_B/Cu^{2+}$ for the $BF_4^-$ salt. The structure appears to be analogous to that of a variety of other copper dimers having low moments.[17,18] The room-temperature ESR spectrum of $[Cu(DAPDH)]_2(BF_4)_2$ (Figure 5) is qualitatively similar to that of other magnetically coupled dimers.[12] A detailed study is currently being carried out.[19]

Finally, it should be pointed out that a number of attempts were made to oxidize the $Cu(DAPDH_2)Cl_2$ complex with peroxide and peroxydisulfate to Cu(III). These efforts were not successful, and there is no evidence that the $DAPDH_2$ ligand stabilizes high oxidation states of copper, as it does in the case of nickel. It should be noted, however, that $Cu(DAPDH_2)Cl_2$ does not have a strong *spherical* crystal field, which was considered by Baucom and Drago[4] to be a requirement for the stabilization of nickel(IV).

**Acknowledgment.** The authors thank Mr. Kevin Howard, Ms. Padmini Chak, and Dr. Robert Nakon for their assistance and comments. We also thank Dr. N. S. Dalal for some of the ESR measurements.

**Registry No.** $[Cu(DAPDH_2)Cl_2]$, 72016-96-7; $[Cu(DAPDH)]_2Cl_2$, 72016-97-8; $[Cu(DAPDH)]_2(BF_4)_2$, 72016-99-0; $DAPDH_2$, 36408-72-7; $NH_2OH{\cdot}HCl$, 5470-11-1; 2,6-diacetylpyridine, 1129-30-2.

---

[16] A detailed magnetic study will be the subject of a future communication.

[17] (a) Whyman, R.; Copley, D.; Hatfield, W. E. *J. Am. Chem. Soc.* **1967**, *89*, 3135. (b) Hatfield, W. E.; Fountain, C.; Whyman, R. *Inorg. Chem.* **1966**, *5*, 1855. (c) Hatfield, W. E.; Muto, Y.; Jonassen, H. B.; Paschal, J. S. *Ibid.* **1965**, *4*, 97.

[18] (a) Countryman, R.; Robinson, W. T.; Sinn, E. *Inorg. Chem.* **1974**, *13*, 2013. (b) Gluvchinsky, P.; Mockler, G.; Healy, P.; Sinn, E. *J. Chem. Soc., Dalton Trans.* **1974**, 1156.

[19] Dalal, N. S.; Nicholson, G. A., to be submitted for publication.

---

Contribution from the Department of Chemistry,
West Virginia University, Morgantown, West Virginia 26506

# Crystal and Molecular Structure of the Dihydrate of a Coupled Copper(II) Dimer Derived from 2,6-Diacetylpyridine Dioxime

GARY A. NICHOLSON, JEFFREY L. PETERSEN,* and B. JACK McCORMICK*

*Received July 6, 1979*

The crystal structure of $[Cu(DAPDH)]_2(BF_4)_2{\cdot}2H_2O$, where $DAPDH_2$ is 2,6-diacetylpyridine dioxime, $C_9H_{11}N_3O_2$, has been determined to establish the mode of oxime coordination. The structural analysis shows that the nearly planar $DAPDH^-$ group behaves as a bridging tetradentate ligand. The distorted square-pyramidal coordination about each copper atom includes the three nitrogen donors from one oxime and one oxygen donor from the other oxime located basally in a distorted square-planar arrangement with a loosely coordinated water molecule occupying the apical position. The copper atoms are displaced ca. 0.2 Å above the respective plane of the four basal donor atoms. The dimer's structure permits a parallel alignment of dication pairs with an interdimer spacing of ca. 3.5 Å in the crystal lattice. However, since the shortest intermolecular Cu⋯Cu separation of 4.495 (1) Å is substantially longer than the intramolecular Cu⋯Cu distance of 3.5453 (7) Å, intermolecular contributions to the electron-exchange interaction are not expected to contribute appreciably to the compound's solid-state magnetic behavior (viz., $\mu_{eff} = 0.6\ \mu_B$ at 295 K). The oxime's unsymmetrical mode of coordination produces averaged metal–ligand bond distances: Cu–N(oxime), 2.073 Å; Cu–N(py), 1.915 Å; Cu–N(deprotonated oxime), 2.026 Å; Cu–O(deprotonated oxime), 1.876 Å. The compound crystallizes in the centrosymmetric $P\bar{1}$ triclinic lattice with refined lattice parameters of $a = 8.251$ (4) Å, $b = 12.268$ (3) Å, $c = 13.411$ (3) Å, $\alpha = 86.62$ (3)°, $\beta = 83.74$ (3)°, $\gamma = 81.11$ (3)°, $V = 1332.0$ (7) Å$^3$, and $Z = 2$. Full-matrix least-squares refinement (based on $F_o^2$) of 3123 diffractometry data with $F_o^2 > \sigma(F_o^2)$ led to final discrepancy indices of $R(F_o) = 0.044$, $R(F_o^2) = 0.057$, $R_w(F_o^2) = 0.098$, and $\sigma_1 = 2.07$.

## Introduction

Structural studies of a wide variety of transition-metal oxime complexes have shown that the oxime ligand can coordinate via several different bonding interactions,[1] which are dependent upon the metal ion, its oxidation state, and the oxime's primary structure. An oxime ligand of particular interest is 2,6-diacetylpyridine dioxime, $DAPDH_2$,[2] which contains three distinct types of potential donor atoms, namely, the oxime N atom, the pyridine N atom, and, after deprotonation, the oxime O atom. The aqueous solution chemistry of iron(II) and

---

[1] Chakravorty, A. *Coord. Chem. Rev.* **1974**, *13*, 1.

[2] Abbreviations which are used in this paper include: $DAPDH_2$, 2,6-diacetylpyridine dioxime, $C_9H_{11}N_3O_2$; PnAO, 2,2′-(1,3-diaminopropane)bis(2-methyl-3-butanone oxime), $C_{13}H_{28}N_4O_2$; EnAO, 2,2′-(1,2-diaminoethane)bis(2-methyl-3-butanone oxime), $C_{12}H_{26}N_4O_2$.

0020-1669/80/1319-0195$01.00/0