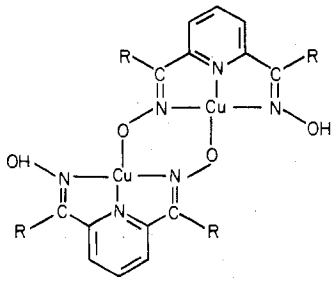
be attributed to dimer formation since, as will be discussed below, the dimers are easily ruptured by coordinating solvents. In addition, it should be emphasized that there was no evidence for dimer formation in the aqueous titration studies.

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.

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

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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), $C_{12}H_{26}N_4O_2$.

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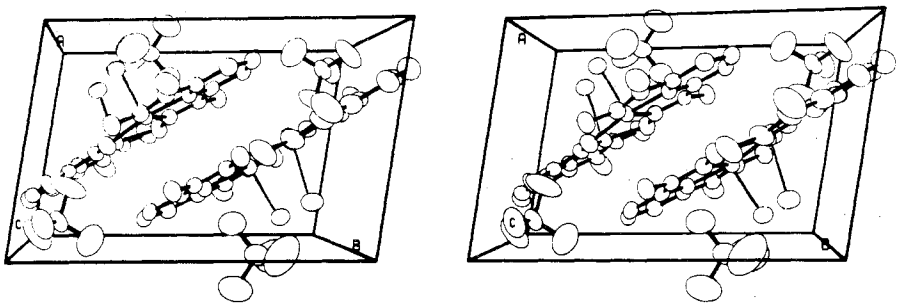

**Figure 1.** Stereoscopic drawing of the molecular arrangement of $[Cu(DAPDH)]_2(BF_4)_2 \cdot 2H_2O$ in the triclinic $P\bar{1}$ unit cell. The binuclear Cu(II) oxime dications are aligned parallel to each other with an interdimer separation of ca. 3.5 Å. The thermal ellipsoids are scaled to enclose 50% probability.

**Table I.** Unit Cell and Space Group Data for $Cu_2(C_9H_{10}N_3O_2)_2(BF_4)_2 \cdot 2H_2O$

| | | | |
|---|---|---|---|
| cryst system | triclinic | $d$(obsd), g/cm$^3$ | 1.77 |
| | | $d$(calcd), g/cm$^3$ | 1.798 |
| $a$, Å | 8.251 (4) | $Z$, molecules/unit cell | 2 |
| $b$, Å | 12.268 (3) | | |
| $c$, Å | 13.411 (3) | $\mu$, cm$^{-1}$ | 17.8 |
| $\alpha$, deg | 86.62 (3) | range of transmissn coeff | 0.837–0.850 |
| $\beta$, deg | 83.74 (3) | | |
| $\gamma$, deg | 81.11 (3) | space group | $P\bar{1}$ ($C_i^1$, No. 2) |
| vol, Å$^3$ | 1332.0 (7) | systematic absences | none |
| fw | 721.12 | | |

$DAPDH_2$ has been described[3] and several complexes of nickel have been reported,[4] but structural data is limited to the formally Ni(IV) complex, $Ni(DAPD)_2$. In this complex Sproul and Stucky[5] found that the two planar $DAPD^{2-}$ ligands coordinate through the nitrogen donors to produce a distorted octahedral environment about the metal. In the previous paper[6] the coordination chemistry of $DAPDH_2$ with Cu(II) is presented and the isolation of both $[Cu(DAPDH_2)Cl_2]$ and $[Cu(DAPDH)]_2^{2+}$ is described. We have undertaken an X-ray diffraction study of $[Cu(DAPDH)]_2(BF_4)_2 \cdot 2H_2O$ to establish the nature of the oxime coordination and its relationship to the dimer's solid-state magnetic behavior.

## Experimental Section

**Crystal Preparation.** $[Cu(DAPDH)]_2(BF_4)_2$ was prepared by previously described methods.[6] Recrystallization from nitromethane in an open container provided dark blue crystals of the dihydrate. The presence of the waters of hydration, which could be removed in vacuo, was confirmed by IR analysis. Attempts to grow crystals of the unhydrated dimer from a nitromethane solution in a desiccator gave only powders.

**Data Collection.** A rectangular crystal of dimensions 0.10 mm × 0.10 mm × 0.25 mm was mounted in a general orientation and transferred to a Picker goniostat under computer control by a Krisel Control diffractometer automation system. A preliminary peak search of low-angle reflections provided a sufficient number of reflections to determine the lattice parameters of the reduced unit cell (Laue symmetry, $C_i$-$\bar{1}$) from the autoindexing routine.[7] From a rough orientation matrix the angular coordinates for higher order reflections were calculated and optimized by the automatic reflection centering routine. The optimized angles ($\omega$, $\chi$, $2\theta$) from 20 centered diffraction peaks within a $2\theta$ range of 25–33° were used to refine the final lattice parameters in Table I. The experimental density was measured by flotation in a $CH_2I_2/CCl_4$ solution.

Intensity data ($h,\pm k,\pm l$) were measured with Zr-filtered Mo K$\alpha$ X-ray radiation ($\lambda$(K$\alpha_1$) 0.709 26 Å, $\lambda$(K$\alpha_2$) 0.713 54 Å) at a takeoff angle of 2° within a Bragg angle range of $3° \leq 2\theta \leq 45°$. The $\theta$–$2\theta$ scan mode was employed to scan each peak at a fixed scan rate of 2°/min. For each peak the scan width was determined from the expression 1.4 + 0.7 tan $\theta$. Background counts of 10-s duration were measured at the extremes of each scan with the stationary-crystal, stationary-counter method. The pulse-height analyzer of the scintillation detector was adjusted to accept 90% of the diffraction peak. During data collection the intensities of two standard reflections were measured after every 120 min of exposure time; their combined intensity decreased by ca. 3.0%. The intensity data were corrected for background, absorption, crystal decay, and Lorentz–polarization effects. The standard deviation for each of the 3797 measured peaks was calculated from the expression $\sigma^2(I) = \sigma_c^2(I) + (0.03I)^2$ where $\sigma_c^2(I) = W^2(S/t_s^2 + B/t_b^2)$ and $I = W(S/t_s - B/t_b)$. In these relationships $S$ represents the total scan count measured in time, $t_s$, $B$ is the combined background count in $t_b$, and $W$ is the scan width. Duplicate reflections were averaged to produce 3501 independent reflections of which 3123 were found to have $F_o^2 \geq \sigma(F_o^2)$. The quality of the X-ray diffraction data is reflected by the agreement factors[8] calculated for equivalent reflections of $R_a(F_o) = 0.016$ and $R_a(F_o^2) = 0.011$.

**Table II.** Intensity Statistics for X-ray Diffraction Data of $Cu_2(C_9H_{10}N_3O_2)_2(BF_4)_2 \cdot 2H_2O$

| | | theoret | |
|---|---|---|---|
| | exptl | centrosym | non-centrosym |
| $E^2$ | 1.000 | 1.000 | 1.000 |
| MOD($E^2 - 1$) | 0.933 | 0.968 | 0.736 |
| MOD($E$) | 0.817 | 0.798 | 0.886 |

**Structure Analysis.** Approximate positions for nearly half of the nonhydrogen atoms (including the two independent Cu atoms) were interpolated from the first $E$ map calculated by using the phase assignments for the set with the highest figure of merit from MULTAN 78.[9] The intensity statistics in Table II verify that the compound crystallizes in the centrosymmetric $P\bar{1}$ space group. The remaining nonhydrogen atoms were located from subsequent Fourier analyses. Examination of the agreement between $F_o$ and $F_c$ indicated a small systematic variation due to extinction, and an isotropic secondary extinction parameter, $g$,[10–12] was introduced. Full-matrix refinement of the positional and anisotropic thermal parameters for the 42 nonhydrogen atoms with fixed contributions[13] from the 24 hydrogen atoms led to the final discrepancy values[14–18] of $R(F_o) = 0.044$, $R(F_o^2)$

(3) Hanania, G. I. H.; Irvine, D. H.; Shurayh, F. *J. Chem. Soc.* **1965**, 1149.
(4) Baucom, E. I.; Drago, R. S. *J. Am. Chem. Soc.* **1971**, *93*, 6469.
(5) Sproul, G.; Stucky, G. *Inorg. Chem.* **1973** *12*, 2899.
(6) Nicholson, G. A.; Lazarus, C. R.; McCormick, B. J. *Inorg. Chem.*, preceding paper in this issue.
(7) The automatic indexing algorithm is based upon Jacobson's procedure: Jacobson, R. A. *J. Appl. Crystallogr.* **1976**, *9*, 115.
(8) $R_a(F_o) = \sum|F_o(\text{av}) - |F_o||/\sum F_o$ and $R_a(F_o^2) = \sum|F_o^2(\text{av}) - F_o^2|/\sum F_o^2$.
(9) Declerq, J. P.; Germain, D.; Main, P.; Woolfson, M. M. *Acta Crystallogr., Sect. A* **1973**, *29*, 231.
(10) The Zachariasen approximation[11] was used for the overall isotropic extinction parameter, $g$, as defined and scaled by Coppens and Hamilton.[12]
(11) Zachariasen, W. H. *Acta Crystallogr.* **1967**, *23*, 558.
(12) Coppens, P.; Hamilton, W. C. *Acta Crystallogr., Sect. A* **1970**, *26*, 71.
(13) All of the hydrogen atoms were located by difference Fourier methods. Their positions were refined with isotropic temperature factors set at 5.0 Å$^2$ for the pyridine-ring hydrogens and 8.0 Å$^2$ for the remaining ones. During the refinement the positional and thermal parameters for the nonhydrogen atoms were held constant. Alternate cycles of varying only the hydrogen positions and only the nonhydrogen atom parameters were performed until convergence.

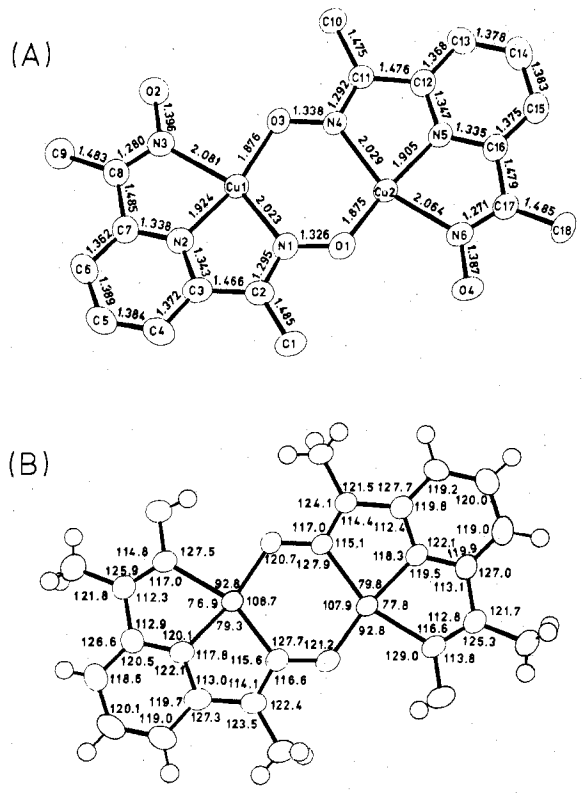


**Figure 2.** Molecular configurations of the $[Cu(DAPDH)]_2^{2+}$ dication with the nonhydrogen atom labeling scheme and bond distances given in (A) and bond angles in (B). These structural parameters reflect the twofold symmetry of the dication. The oxime hydrogen atoms are included in (B).

= 0.057, and $R_w(F_o^2) = 0.098$ with $\sigma_1 = 2.07$ and $g = (0.9\ (6)) \times 10^{-5}$. At the conclusion of the refinement, the shift to error ratio for the varied parameters was less than 10%. A final difference Fourier map revealed a residual peak of 0.7 e/Å$^3$ in the vicinity of the second $BF_4^-$ anion.

The positional and anisotropic thermal parameters obtained from the last least-squares cycle for the nonhydrogen atoms are given in Table III. Structure factor tables, the hydrogen atom positions and structural parameters are available in the supplementary material. Selected interatomic distances and bond angles with esd's calculated from the errors in the fractional atomic coordinates are presented in Table IV. Least-squares planes of interest are provided in Table V.[19]

## Results and Discussion

**Description of the Crystal Structure.** The crystal structure of $Cu_2(C_9H_{10}N_3O_2)_2(BF_4)_2 \cdot 2H_2O$ or $[Cu(DAPDH)]_2(BF_4)_2 \cdot 2H_2O$ is depicted stereographically in Figure 1, which shows the arrangement of the two binuclear copper(II) cations, four $BF_4^-$ monoanions, and four waters of hydration in the centrosymmetric triclinic unit cell. The basic structure of the hydrated $[Cu(DAPDH)]_2^{2+}$ dication resembles two square pyramids joined at one edge. The basal planes formed by the dioxime ligands intersect at a dihedral angle of 169.6°. The dimer's relatively planar structure permits the cations to align in a parallel fashion with an interdimer spacing of ca. 3.5 Å. Since the shortest intermolecular Cu···Cu separation of 4.495 (1) Å is considerably longer than the intramolecular Cu(1)···Cu(2) separation of 3.5453 (7) Å, intermolecular contributions to the electron-exchange interaction are not expected to contribute appreciably to the dimer's solid-state magnetic behavior.[6] Although the dication's geometry is not constrained crystallographically, a comparison of the structural parameters, as given in Figure 2 with the atom-labeling scheme, demonstrates that its structure possesses nearly twofold symmetry. The corresponding bond distances and angles for the two halves of the dimer are equivalent within experimental error.

The structures of the two independent tetrahedral $BF_4^-$ anions are fairly well-defined except for an abnormally short B(2)–F(6) bond distance in one of the tetrafluoroborate anions. The range of F–B–F bond angles and B–F bond distances is reasonably small considering the difficulty that is normally incurred when the highly symmetrical $BF_4^-$ species is employed as a counterion. The possibility of weak hydrogen bonding between the fluorine atoms and the water molecules is suggested by several H···F separations of ca. 1.9 Å.

**Nature of the Metal–Oxime Interaction.** Details of the coordination chemistry of 2,6-diacetylpyridine dioxime, $DAPDH_2$, were initially examined by Drago and Baucom,[4] who used the deprotonated form to stabilize the high metal oxidation state in $Ni(DAPD)_2$. Sproul and Stucky[5] structurally characterized this complex and observed that the dioxime behaves as a tridentate ligand that produces a distorted octahedral environment about the Ni(IV) metal ion. To accommodate the Ni(IV) ion's small size, the deprotonated oxime groups are pulled toward the metal, causing a noticeable closing of several chelate angles from the ideal value of 120° required for $sp^2$ hybridization.

In contrast to the Ni(IV) complex,[5] the dioxime ligand in the hydrated $[Cu(DAPDH)]_2^{2+}$ dication behaves as a tetradentate ligand. Each copper center is surrounded by two N(oxime) and the N(py) donors from the oxime, analogous to the oxime ligand bonding in $Cu(DAPDH)_2Cl_2$ and $Ni(DAPD)_2$; in addition, each copper ion is coordinated to an O(oxime) donor from the adjacent oxime ligand to give a distorted square-planar basal arrangement about each copper. Cu(1) and Cu(2) are displaced 0.195 (1) and 0.186 (1) Å above the respective plane containing the four planar oxime donor atoms. The dioxime ligands are not strictly planar, as evidenced by the perpendicular displacements calculated for the ligand's carbon and oxygen atoms from the corresponding least-squares plane defined by the three nitrogen donors. For both oxime ligands, these atoms are located between 0.1 and 0.4 Å below the plane and away from the coordinated copper atoms. A water molecule is located above each copper atom, with an O···O separation of 2.922 (5) Å. The Cu–$OH_2$ distances are 2.249 (3) and 2.317 (4) Å. These Cu(II)–$OH_2$ distances can be compared to the corresponding distance of 2.339 Å in $Cu(NH_3)_4H_2O^{2+}$, in which the water is considered to be bonded.[20] On this basis the copper centers in $Cu(DAPDH)_2(H_2O)_2^{2+}$ can be best described as having a distorted square-pyramidal coordination geometry with water

(14) The least-squares refinement[15] of the X-ray diffraction data was based upon the minimization of $\sum w_i|F_o^2 - S^2F_c^2|$, where $w_i$ is the individual weighting factor and $S$ is the scale factor. The discrepancy indices were calculated from the expressions $R(F_o) = \sum||F_o| - |F_c||/\sum|F_o|$, $R(F_o^2) = \sum|F_o^2 - F_c^2|/\sum F_o^2$, and $R_w(F_o^2) = [\sum w_i|F_o^2 - F_c^2|^2/\sum w_iF_o^4]^{1/2}$. The standard deviation of an observation of unit weight is $\sigma_1 = [\sum w_i|F_o^2 - F_c^2|/(n - p)]^{1/2}$ where $n$ is the number of observations and $p$ is the number of parameters varied (viz., 380) during the last refinement cycle. The corresponding data to parameter ratio for 3123 data with $F_o^2 > \sigma(F_o^2)$ is 8.2:1.

(15) The scattering factors utilized in all calculations were those of Cromer and Mann[16] for the nonhydrogen atoms and those of Stewart et al.[17] for the hydrogen atoms with corrections included for anomalous dispersion.

(16) Cromer, D. T.; Mann, J. *Acta Crystallogr., Sect. A* **1968**, 24, 231.
(17) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965** *42*, 3175.
(18) Cromer, D. T.; Liberman, D. *J. Chem. Phys.* **1970** *53*, 1891.

(19) The computer programs which were used to perform the X-ray diffraction data analysis with their accession names in the World List of Crystallographic Computer Programs are as follows: data reduction and absorption correction, DATALIB; data averaging and sorting, DATASORT; Fourier summation, CNTFOR; modification of FORDAP; direct-methods analysis, MULTAN (1978 version); least-squares refinement, OR XFLS3; error analysis of distances and angles, OR FEE3; structure plotting, ORTEP II. Least-squares planes were calculated with the program PLNJO based upon the method of Blow: Blow, D. *Acta Crystallogr.* **1960**, *13*, 168.

(20) Morosin, B. *Acta Crystallogr., Sect. B* **1969**, *25*, 19.

**Table III.** Positional Parameters and Thermal Factors for Nonhydrogen Atoms in $Cu_2(C_9H_{10}N_3O_2)_2(BF_4)_2 \cdot 2H_2O$[a,b]

(A) Positional Parameters

| atom | x | y | z | atom | x | y | z |
|---|---|---|---|---|---|---|---|
| Cu(1) | 0.37599 (7) | 0.67424 (5) | 0.47412 (4) | C(8) | 0.2883 (6) | 0.6254 (4) | 0.6852 (4) |
| Cu(2) | 0.49545 (7) | 0.75608 (5) | 0.22224 (4) | C(9) | 0.2483 (8) | 0.6325 (5) | 0.7954 (4) |
| N(1) | 0.3706 (5) | 0.5919 (3) | 0.3485 (3) | C(10) | 0.7018 (7) | 0.9481 (5) | 0.4173 (4) |
| N(2) | 0.2736 (5) | 0.5504 (3) | 0.5295 (3) | C(11) | 0.6398 (6) | 0.8959 (4) | 0.3357 (3) |
| N(3) | 0.3693 (5) | 0.6900 (3) | 0.6282 (3) | C(12) | 0.6767 (6) | 0.9307 (4) | 0.2295 (3) |
| N(4) | 0.5542 (5) | 0.8156 (3) | 0.3495 (3) | C(13) | 0.7667 (6) | 1.0112 (4) | 0.1918 (4) |
| N(5) | 0.6162 (5) | 0.8694 (3) | 0.1663 (3) | C(14) | 0.7959 (7) | 1.0275 (5) | 0.0892 (4) |
| N(6) | 0.5007 (5) | 0.7363 (4) | 0.0701 (3) | C(15) | 0.7370 (7) | 0.9612 (5) | 0.0258 (4) |
| O(1) | 0.4275 (4) | 0.6184 (3) | 0.2554 (2) | C(16) | 0.6472 (6) | 0.8811 (4) | 0.0668 (4) |
| O(2) | 0.4222 (5) | 0.7732 (3) | 0.6775 (2) | C(17) | 0.5817 (6) | 0.7989 (5) | 0.0121 (4) |
| O(3) | 0.5157 (4) | 0.7813 (3) | 0.4445 (2) | C(18) | 0.6202 (9) | 0.7884 (6) | −0.0979 (4) |
| O(4) | 0.4471 (5) | 0.6541 (3) | 0.0212 (3) | B(1) | 0.1378 (8) | 0.1148 (5) | 0.3252 (4) |
| WO(5) | 0.1403 (4) | 0.7898 (3) | 0.4561 (3) | B(2) | 0.0131 (10) | 0.6887 (7) | 0.0843 (6) |
| WO(6) | 0.2261 (5) | 0.8456 (3) | 0.2441 (3) | F(1) | 0.1338 (5) | 0.0726 (3) | 0.2343 (2) |
| C(1) | 0.2728 (7) | 0.4400 (4) | 0.2752 (4) | F(2) | 0.0705 (5) | 0.0503 (3) | 0.3988 (2) |
| C(2) | 0.2970 (6) | 0.5054 (4) | 0.3607 (4) | F(3) | 0.2936 (5) | 0.1255 (4) | 0.3406 (3) |
| C(3) | 0.2407 (6) | 0.4786 (4) | 0.4655 (4) | F(4) | 0.0497 (6) | 0.2175 (4) | 0.3279 (4) |
| C(4) | 0.1651 (6) | 0.3902 (4) | 0.5017 (4) | F(5) | 0.1445 (5) | 0.6078 (3) | 0.0941 (3) |
| C(5) | 0.1234 (7) | 0.3774 (4) | 0.6040 (4) | F(6) | 0.0226 (7) | 0.7440 (4) | 0.0010 (4) |
| C(6) | 0.1609 (6) | 0.4522 (4) | 0.6686 (4) | F(7) | −0.1287 (6) | 0.6444 (4) | 0.0972 (4) |
| C(7) | 0.2365 (6) | 0.5384 (4) | 0.6288 (4) | F(8) | −0.0043 (7) | 0.7521 (5) | 0.1637 (5) |

(B) Temperature Factors

| atom | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|---|---|---|---|---|---|---|
| Cu(1) | 444 (4) | 389 (4) | 333 (4) | −114 (3) | −31 (3) | −43 (3) |
| Cu(2) | 435 (4) | 493 (4) | 315 (4) | −159 (3) | −35 (3) | −62 (3) |
| N(1) | 444 (25) | 412 (24) | 356 (24) | −93 (20) | −29 (19) | −48 (18) |
| N(2) | 426 (25) | 391 (23) | 434 (26) | −75 (19) | −57 (19) | −35 (19) |
| N(3) | 475 (26) | 430 (24) | 397 (24) | −108 (21) | −63 (20) | −57 (20) |
| N(4) | 377 (23) | 439 (23) | 301 (23) | −110 (20) | −45 (17) | −41 (18) |
| N(5) | 457 (25) | 522 (25) | 323 (23) | −148 (21) | −34 (19) | −58 (19) |
| N(6) | 499 (27) | 725 (31) | 376 (24) | −251 (25) | −10 (21) | −150 (23) |
| O(1) | 623 (23) | 492 (21) | 358 (20) | −159 (18) | −24 (17) | −116 (16) |
| O(2) | 684 (25) | 556 (22) | 483 (21) | −254 (20) | −46 (18) | −103 (17) |
| O(3) | 540 (22) | 563 (21) | 298 (19) | −216 (18) | −50 (16) | −12 (16) |
| O(4) | 836 (30) | 984 (32) | 501 (23) | −498 (26) | 8 (21) | −272 (22) |
| WO(5) | 536 (23) | 542 (22) | 574 (23) | −40 (18) | −17 (18) | 0 (18) |
| WO(6) | 557 (24) | 602 (24) | 814 (28) | −92 (20) | −124 (21) | −131 (20) |
| C(1) | 655 (37) | 481 (31) | 500 (32) | −165 (28) | −101 (27) | −95 (25) |
| C(2) | 419 (29) | 353 (28) | 457 (30) | −48 (24) | −58 (23) | −70 (22) |
| C(3) | 398 (29) | 339 (27) | 534 (32) | −9 (23) | −111 (24) | −69 (24) |
| C(4) | 501 (33) | 367 (29) | 633 (38) | −103 (26) | −101 (27) | 10 (25) |
| C(5) | 551 (35) | 384 (29) | 685 (39) | −161 (26) | −104 (29) | 111 (27) |
| C(6) | 489 (33) | 552 (33) | 453 (31) | −115 (28) | −30 (25) | 80 (26) |
| C(7) | 384 (29) | 446 (30) | 425 (31) | −55 (24) | −42 (23) | 54 (24) |
| C(8) | 420 (30) | 482 (30) | 393 (30) | −78 (26) | −43 (24) | −22 (24) |
| C(9) | 797 (44) | 834 (43) | 404 (33) | −323 (36) | 23 (30) | −47 (29) |
| C(10) | 630 (37) | 742 (38) | 411 (30) | −354 (31) | −99 (27) | −54 (27) |
| C(11) | 386 (28) | 448 (29) | 331 (27) | −109 (24) | −46 (22) | −50 (22) |
| C(12) | 383 (28) | 517 (31) | 369 (28) | −67 (25) | −7 (23) | −72 (24) |
| C(13) | 520 (33) | 508 (32) | 503 (33) | −226 (28) | 6 (25) | −61 (25) |
| C(14) | 703 (41) | 703 (39) | 510 (36) | −347 (33) | 66 (30) | 4 (29) |
| C(15) | 688 (40) | 811 (42) | 355 (31) | −254 (35) | 48 (28) | 37 (29) |
| C(16) | 444 (31) | 685 (36) | 332 (29) | −160 (28) | 4 (23) | −48 (25) |
| C(17) | 487 (33) | 740 (38) | 344 (29) | −216 (30) | −5 (25) | −86 (27) |
| C(18) | 937 (51) | 1457 (65) | 391 (34) | −645 (48) | 74 (33) | −226 (37) |
| B(1) | 638 (44) | 563 (41) | 372 (35) | −313 (35) | −17 (30) | −73 (30) |
| B(2) | 624 (51) | 780 (53) | 706 (52) | −224 (44) | −97 (39) | 43 (44) |
| F(1) | 1229 (31) | 809 (24) | 419 (18) | −477 (23) | −15 (19) | −80 (16) |
| F(2) | 1347 (36) | 1376 (34) | 492 (21) | −958 (30) | 31 (21) | 54 (21) |
| F(3) | 845 (28) | 1925 (46) | 684 (25) | −775 (30) | −196 (21) | 227 (26) |
| F(4) | 1455 (44) | 969 (34) | 1458 (43) | 112 (32) | −131 (35) | −326 (30) |
| F(5) | 720 (27) | 1012 (30) | 1485 (39) | −142 (24) | −256 (25) | 440 (27) |
| F(6) | 1727 (51) | 1529 (44) | 1322 (41) | 344 (39) | 571 (37) | 934 (36) |
| F(7) | 873 (32) | 1636 (47) | 1707 (48) | −481 (32) | −397 (31) | 596 (37) |
| F(8) | 1467 (49) | 2103 (61) | 1761 (56) | −68 (45) | −512 (42) | −1013 (50) |

[a] The estimated standard deviations in parentheses for this and all subsequent tables refer to the least-significant figures. [b] The form of the anisotropic temperature factors is $\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^*b^*U_{12} + 2hla^*c^*U_{13} + 2klb^*c^*U_{23})]$. The components of the anisotropic temperature factors have been multiplied by $10^4$.

molecules in the apical positions. However, the apical bonding must be very weak, as both of the water molecules are removed by pumping the sample at ambient temperature. It should also be pointed out that the $H_2O$–Cu bond distances are ca. 0.5 Å longer than the Cu–O(oxime) distances, again emphasizing the weakness of the copper–water interaction. The $H_2O$–Cu

**Table IV.** Interatomic Distances (Å) and Bond Angles (Deg) for $Cu_2(C_9H_{10}N_3O_2)_2(BF_4)_2 \cdot 2H_2O$[a]

(A) Bond Distances

| | | | |
|---|---|---|---|
| Cu(1)-N(1) | 2.023 (4) | Cu(2)-N(4) | 2.029 (4) |
| Cu(1)-N(2) | 1.924 (4) | Cu(2)-N(5) | 1.905 (4) |
| Cu(1)-N(3) | 2.081 (4) | Cu(2)-N(6) | 2.064 (4) |
| Cu(1)-O(3) | 1.876 (4) | Cu(2)-O(1) | 1.875 (3) |
| Cu(1)-WO(5) | 2.249 (3) | Cu(2)-WO(6) | 2.317 (4) |
| N(1)-O(1) | 1.326 (5) | N(4)-O(3) | 1.338 (5) |
| N(1)-C(2) | 1.295 (6) | N(4)-C(11) | 1.292 (6) |
| C(1)-C(2) | 1.485 (7) | C(10)-C(11) | 1.475 (8) |
| C(2)-C(3) | 1.466 (7) | C(11)-C(12) | 1.476 (6) |
| C(3)-N(2) | 1.343 (7) | C(12)-N(5) | 1.347 (7) |
| C(3)-C(4) | 1.372 (7) | C(12)-C(13) | 1.368 (7) |
| C(4)-C(5) | 1.384 (8) | C(13)-C(14) | 1.378 (7) |
| C(5)-C(6) | 1.389 (8) | C(14)-C(15) | 1.383 (9) |
| C(6)-C(7) | 1.362 (7) | C(15)-C(16) | 1.375 (8) |
| C(7)-N(2) | 1.338 (6) | C(16)-N(5) | 1.335 (6) |
| C(7)-C(8) | 1.485 (7) | C(16)-C(17) | 1.479 (8) |
| C(8)-C(9) | 1.483 (7) | C(17)-C(18) | 1.485 (8) |
| C(8)-N(3) | 1.280 (6) | C(17)-N(6) | 1.271 (7) |
| N(3)-O(2) | 1.396 (6) | N(6)-O(4) | 1.387 (7) |
| B(1)-F(1) | 1.358 (7) | B(2)-F(5) | 1.364 (8) |
| B(1)-F(2) | 1.354 (7) | B(2)-F(6) | 1.274 (10) |
| B(1)-F(3) | 1.351 (8) | B(2)-F(7) | 1.355 (10) |
| B(1)-F(4) | 1.355 (8) | B(2)-F(8) | 1.338 (10) |

(B) Bond Angles

| | | | |
|---|---|---|---|
| N(1)-Cu(1)-N(2) | 79.3 (2) | N(4)-Cu(2)-N(5) | 79.8 (2) |
| N(1)-Cu(1)-N(3) | 154.8 (2) | N(4)-Cu(2)-N(6) | 157.3 (2) |
| N(1)-Cu(1)-O(3) | 108.7 (1) | N(4)-Cu(2)-O(1) | 107.9 (1) |
| N(1)-Cu(1)-WO(5) | 95.2 (1) | N(4)-Cu(2)-WO(6) | 92.7 (1) |
| N(2)-Cu(1)-N(3) | 76.9 (2) | N(5)-Cu(2)-N(6) | 77.8 (2) |
| N(2)-Cu(1)-O(3) | 164.9 (2) | N(5)-Cu(2)-O(1) | 163.0 (1) |
| N(2)-Cu(1)-WO(5) | 96.2 (1) | N(5)-Cu(2)-WO(6) | 103.5 (1) |
| N(3)-Cu(1)-O(3) | 92.8 (2) | N(6)-Cu(2)-O(1) | 92.8 (2) |
| N(3)-Cu(1)-WO(5) | 95.6 (1) | N(6)-Cu(2)-WO(6) | 96.1 (2) |
| O(3)-Cu(1)-WO(5) | 95.8 (1) | O(1)-Cu(2)-WO(6) | 91.6 (1) |
| Cu(1)-N(1)-O(1) | 127.7 (3) | Cu(2)-N(4)-O(3) | 127.9 (3) |
| Cu(2)-O(1)-N(1) | 121.2 (3) | Cu(1)-O(3)-N(4) | 120.7 (3) |
| Cu(1)-N(1)-C(2) | 115.6 (3) | Cu(2)-N(4)-C(11) | 115.1 (3) |
| O(1)-N(1)-C(2) | 116.6 (4) | O(3)-N(4)-C(11) | 117.0 (4) |
| C(1)-C(2)-N(1) | 122.4 (4) | C(10)-C(11)-N(4) | 124.1 (4) |
| N(1)-C(2)-C(3) | 114.1 (4) | N(4)-C(11)-C(12) | 114.4 (4) |
| C(1)-C(2)-C(3) | 123.5 (4) | C(10)-C(11)-C(12) | 121.5 (4) |
| C(2)-C(3)-N(2) | 113.0 (4) | C(11)-C(12)-N(5) | 112.4 (4) |
| N(2)-C(3)-C(4) | 119.7 (4) | N(5)-C(12)-C(13) | 119.8 (4) |
| C(2)-C(3)-C(4) | 127.3 (5) | C(11)-C(12)-C(13) | 127.7 (5) |
| C(3)-C(4)-C(5) | 119.0 (5) | C(12)-C(13)-C(14) | 119.2 (5) |
| C(4)-C(5)-C(6) | 120.1 (5) | C(13)-C(14)-C(15) | 120.0 (5) |
| C(5)-C(6)-C(7) | 118.6 (5) | C(14)-C(15)-C(16) | 119.0 (5) |
| C(6)-C(7)-N(2) | 120.5 (5) | C(15)-C(16)-N(5) | 119.9 (5) |
| N(2)-C(7)-C(8) | 112.9 (4) | N(5)-C(16)-C(17) | 113.1 (5) |
| C(6)-C(7)-C(8) | 126.6 (4) | C(15)-C(16)-C(17) | 127.0 (5) |
| C(7)-C(8)-N(3) | 112.3 (4) | C(16)-C(17)-N(6) | 112.8 (4) |
| N(3)-C(8)-C(9) | 125.9 (5) | N(6)-C(17)-C(18) | 125.3 (6) |
| C(7)-C(8)-C(9) | 121.8 (5) | C(16)-C(17)-C(18) | 121.7 (5) |
| C(8)-N(3)-O(2) | 114.8 (4) | C(17)-N(6)-O(4) | 113.8 (4) |
| C(8)-N(3)-Cu(1) | 117.0 (4) | C(17)-N(6)-Cu(2) | 116.6 (4) |
| Cu(1)-N(3)-O(2) | 127.5 (3) | Cu(2)-N(6)-O(4) | 129.0 (3) |
| F(1)-B(1)-F(2) | 110.0 (5) | F(5)-B(2)-F(6) | 113.6 (6) |
| F(1)-B(1)-F(3) | 110.8 (5) | F(5)-B(2)-F(7) | 109.9 (6) |
| F(1)-B(1)-F(4) | 109.5 (5) | F(5)-B(2)-F(8) | 108.1 (7) |
| F(2)-B(1)-F(3) | 111.1 (5) | F(6)-B(2)-F(7) | 110.2 (7) |
| F(2)-B(1)-F(4) | 108.7 (5) | F(6)-B(2)-F(8) | 112.8 (7) |
| F(3)-B(1)-F(4) | 106.6 (6) | F(7)-B(2)-F(8) | 101.6 (6) |

(C) Other Interatomic Distances

| | | | |
|---|---|---|---|
| Cu(1)···Cu(2) | 3.5453 (7) | WO(5)···WO(6) | 2.922 (5) |

[a] The esd's given in parentheses for the interatomic separations and bond angles were calculated from the standard errors in the fractional coordinates of the corresponding atomic positions.

bonds are not quite perpendicular to the oxime planes, as the $H_2O$–Cu–N(oxime) and $H_2O$–Cu–N(py) bond angles vary between 91.6 (1) and 103.5 (1)°. The water molecules are not properly orientated for hydrogen bonding with the coordinated $(DAPDH)^-$ moieties.

Similar square-pyramidal ligand dispositions about Cu(II) ions have been observed for monomeric, dimeric, and trimeric oxime species by Schlemper and co-workers, who have determined the crystal structures of $[Cu(PnAO\text{-}H)(ReO_4)]$,[21] $[Cu(EnAO\text{-}H)]_2(ClO_4)_2$,[22] and $[Cu_3(C_8H_{17}N_2O)_3(H_2O)_3OH_{1/2}](ClO_4)_{3/2} \cdot 4H_2O$.[23] In both of the dioxime compounds the two N(oxime) and two N(amine) atoms of the tetradentate α-amine oxime ligand comprise the base of a square pyramid. In the monomeric perrhenate salt, the apical

**Table V.** Equations of "Best" Least-Squares Planes, Perpendicular Distances (Å) from These Planes, and Dihedral Angles between These Planes in the Hydrated $Cu_2(C_9H_{10}N_3O_2)_2^{2+}$ Cation[a,b]

(A) Plane I through N(1), N(2), N(3), and O(3)

$$-6.4457x + 5.9871y - 2.1281z - 0.4096 = 0$$

| | | | |
|---|---|---|---|
| N(1) | 0.004 (4) | N(4) | 0.158 (4) |
| N(2) | −0.005 (5) | N(5) | 0.470 (4) |
| N(3) | 0.005 (5) | N(6) | 0.623 (5) |
| O(3) | −0.003 (4) | O(1) | −0.006 (4) |
| Cu(1) | 0.195 (1) | Cu(2) | 0.451 (1) |
| WO(5) | 2.445 (4) | WO(6) | 2.676 (4) |

(B) Plane II through N(4), N(5), N(6), and O(1)

$$-6.9141x + 4.9923y - 0.1837z - 0.1224 = 0$$

| | | | |
|---|---|---|---|
| N(1) | 0.207 (4) | N(4) | 0.054 (4) |
| N(2) | 0.637 (4) | N(5) | −0.074 (4) |
| N(3) | 0.654 (5) | N(6) | 0.079 (5) |
| O(3) | 0.131 (4) | O(1) | −0.038 (4) |
| Cu(1) | 0.557 (1) | Cu(2) | 0.186 (1) |
| WO(5) | 2.767 (4) | WO(6) | 2.491 (4) |

(C) Plane III through O(1), N(1), O(3), and N(4)

$$-6.7022x + 5.4984y - 1.5855z - 0.1692 = 0$$

| | | | |
|---|---|---|---|
| N(1) | 0.049 (4) | N(4) | 0.048 (4) |
| N(2) | 0.185 (4) | N(5) | 0.218 (4) |
| N(3) | 0.154 (5) | N(6) | 0.413 (5) |
| O(3) | −0.035 (4) | O(1) | −0.039 (4) |
| Cu(1) | 0.267 (1) | Cu(2) | 0.316 (1) |
| WO(5) | 2.510 (4) | WO(6) | 2.578 (4) |

(D) Plane IV through N(1), N(2), and N(3)

$$-6.4741x + 5.9311y - 2.1113z - 0.3755 = 0$$

| | | | |
|---|---|---|---|
| N(1) | −0.001 (4) | C(1) | −0.113 (6) |
| N(2) | 0.001 (4) | C(2) | −0.062 (5) |
| N(3) | −0.001 (4) | C(3) | −0.079 (5) |
| Cu(1) | 0.189 (1) | C(4) | −0.189 (6) |
| Cu(2) | 0.433 (1) | C(5) | −0.212 (6) |
| O(1) | −0.015 (4) | C(6) | −0.147 (6) |
| O(2) | 0.047 (4) | C(7) | −0.041 (5) |
| WO(5) | 2.438 (4) | C(8) | 0.021 (5) |
| WO(6) | 2.661 (4) | C(9) | 0.089 (7) |

(E) Plane V through N(4), N(5), and N(6)

$$-6.4987x + 5.9683y - 0.4508z - 1.1091 = 0$$

| | | | |
|---|---|---|---|
| N(4) | 0.001 (4) | C(10) | −0.200 (6) |
| N(5) | −0.001 (4) | C(11) | −0.071 (5) |
| N(6) | 0.001 (5) | C(12) | −0.056 (5) |
| Cu(1) | 0.258 (1) | C(13) | −0.143 (6) |
| Cu(2) | 0.084 (1) | C(14) | −0.190 (7) |
| O(3) | 0.002 (4) | C(15) | −0.174 (7) |
| O(4) | −0.121 (5) | C(16) | −0.087 (6) |
| WO(5) | 2.488 (4) | C(17) | −0.128 (6) |
| WO(6) | 2.358 (4) | C(18) | −0.391 (8) |

Dihedral Angles (Deg) between Planes

| | | | |
|---|---|---|---|
| I and II | 169.6 | II and IV | 169.9 |
| I and III | 176.2 | II and V | 174.7 |
| I and IV | 179.7 | III and IV | 176.5 |
| I and V | 172.7 | III and V | 174.8 |
| II and III | 173.2 | IV and V | 172.8 |

[a] The equations of the planes are expressed in triclinic fractional coordinates $x$, $y$, and $z$. [b] The positional parameters used in the calculation of a given plane were weighted according to the esd's associated with fractional coordinates.

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(22) Gavel, D. P.; Schlemper, E. O. *Inorg. Chem.* **1979**, *18*, 283.
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position is occupied by an O atom of the perrhenate ion whereas in the binuclear complex the apex is occupied by an O(oxime) atom from the other oxime ligand. The Cu atom is displaced 0.24 and 0.40 Å, respectively, from the tetradentate oxime molecular plane toward the coordinated O atom. The trinuclear species[23] is of particular interest because of its low magnetic moment (<1 $\mu_B$) and the similarity of the oxime-bonding mode to that observed in the $[Cu(DAPDH)]_2^{2+}$ dication. In the trinuclear complex the Cu atoms are arranged in an equilaterial triangle (Cu···Cu = 3.246 Å) which is triply bridged by an oxygen atom. The square-planar coordination about each copper atom includes the N(amine) and N(oxime) donors from one monooxime ligand, a deprotonated O(oxime) donor from another ligand, and the central bridging O atom. A perchlorate ion and a water molecule weakly interact above and below the square plane. In both this trimer[23] and our dimeric complex, the oxime ligand behaves as a bridging group between the Cu centers. The much larger Cu–O(oxime) distance of 1.94 (1) Å in the former is probably a consequence of the trimeric geometry. An analogous trinuclear structure has been observed by Beckett and Hoskins for $[Cu_3(C_6H_6N_2O)_3(OH)](SO_4)\cdot 16.3H_2O$.[24]

The central structure of $[Cu(DAPDH)]_2^{2+}$ (Figure 2) consists of a nearly planar six-membered ring comprised of two Cu oxime units linked by a pair of relatively short Cu–O(oxime) bonds of 1.876 Å (average). This arrangement sharply contrasts to that observed for the highly puckered-ring structure of the $[Cu(EnAO\text{-}H)]_2^{2+}$ dication[22] in which the relatively planar $\alpha$-amine oxime ligands are oriented nearly perpendicular to the central ring. The orbital hybridization about the chelate's O and N donor atoms is nearly $sp^2$. However, as observed in $Ni(DAPD)_2$,[5] appreciable deviations of the M–N–O, M–N–C, N–C–C, and C–N–C bond angles from 120° occur upon metal complexation. Because of the smaller ionic radius of Ni(IV) relative to that of Cu(II), the closing of the chelate angles is more pronounced in the nickel complex. Coordination also distorts the oxime's pyridine ring by opening the corresponding C–N–C bond angle from 116.8[25] to 122.1° (average) in $[Cu(DAPDH)]_2^{2+}$ to 125.3 (4)° in $Ni(DAPD)_2$. Deprotonation of the O(oxime) atom is accompanied by a 0.06 Å (average) reduction of the N–O bond distance from 1.39 Å (N–OH) to 1.33 Å ($N\text{–}O^-$) in the $DAPDH^-$ ligand. For the doubly deprotonated $DAPD^{2-}$ ligand in $Ni(DAPD)_2$, a substantially shorter N–O distance of 1.257 (3) Å is observed.

In contrast to $Ni(DAPD)_2$ the oxime ligand is coordinated unsymmetrically in the hydrated $[Cu(DAPDH)]_2^{2+}$ cation. For the Cu(II) complex the Cu–N(oxime) distances vary from 2.023 (4) to 2.081 (4) Å with the shorter Cu–N(oxime) distance associated with the N atom of the deprotonated oxime group. In both complexes, however, the corresponding metal–N(py) distances are similarly ca. 0.1 Å shorter than the metal–N(oxime) distances. Schlemper and co-workers have observed the reverse trend, however, for the tetradentate $\alpha$-amine oxime[21,22] and the trinuclear Cu(II) complexes,[23,24] in which the Cu–N(oxime) distances are consistently shorter than the interior Cu–N(amine) distances by 0.03–0.07 Å. These differences presumably reflect the respective geometrical and steric requirements which are imposed on these ligands by metal complexation.

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**Registry No.** $[Cu(DAPDH)]_2(BF_4)_2\cdot 2H_2O$, 72035-43-9.

**Supplementary Material Available:** Tables of structure factors, hydrogen atom positions, and structural parameters (14 pages). Ordering information is given on any current masthead page.

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