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Crystal and Molecular Structures of Bis[μ -9,9,9-trifluoro-8-(trifluoromethyl)-6-methyl-5-azanon-5-ene-1,8-diolato(2-)- μ -O,N,O']-dicopper(II), $\text{Cu}_2\text{C}_{20}\text{H}_{26}\text{F}_{12}\text{N}_2\text{O}_4$, and Bis[μ -8,8,8-trifluoro-7-(trifluoromethyl)-5-methyl-4-azaoct-4-ene-1,7-diolato(2-)- μ -O,N,O']-dicopper(II), $\text{Cu}_2\text{C}_{18}\text{H}_{22}\text{F}_{12}\text{N}_2\text{O}_4$. Effects of Varying Chelate Ring Size on Geometry and Antiferromagnetic Exchange in Di- μ -oxo-Bridged Dinuclear Copper(II) Complexes

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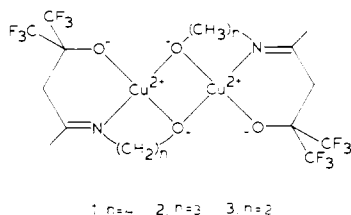
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The crystal and molecular structures of bis[μ -9,9,9-trifluoro-8-(trifluoromethyl)-6-methyl-5-azanon-5-ene-1,8-diolato(2-)- μ -O,N,O']-dicopper(II), $\text{Cu}_2\text{C}_{20}\text{H}_{26}\text{F}_{12}\text{N}_2\text{O}_4$ (**1**), and bis[μ -8,8,8-trifluoro-7-(trifluoromethyl)-5-methyl-4-azaoct-4-ene-1,7-diolato(2-)- μ -O,N,O']-dicopper(II), $\text{Cu}_2\text{C}_{18}\text{H}_{22}\text{F}_{12}\text{N}_2\text{O}_4$ (**2**), have been determined by single-crystal X-ray diffraction methods. Compound **2** conforms to the space group $P2_1/c$ with cell constants $a = 9.144$ (2) Å, $b = 11.364$ (3) Å, $c = 12.008$ (2) Å, $\beta = 97.05$ (10)°, and $V = 1238$ (1) Å³. Refinement based on 1879 reflections with $I > 3\sigma(I)$ gave $R_F = 0.039$ and $R_{wF} = 0.061$. Compound **1** is $Pbca$ with $a = 12.486$ (3) Å, $b = 19.387$ (4) Å, $c = 10.754$ (2) Å, and $V = 2603$ (2) Å³. Least-squares refinement using 1905 reflections with $I > 3\sigma(I)$ gave $R_F = 0.032$ and $R_{wF} = 0.045$. Both structures are dinuclear with the halves related by a center of symmetry. Cu-Cu distances are 2.995 (2) Å for **2** and 3.014 Å for **1**. The structural data are considered with respect to several theories which attempt to explain diamagnetic interactions in dinuclear copper(II) complexes, and the idea that trigonality about the bridging oxygen may be important in these interactions is supported.

Introduction

The phenomenon of antiferromagnetic interaction between copper(II) ions has received considerable attention in recent years.² Small molecules in which spin pairing occurs may serve as models for the copper(II) sites in biological systems, specifically, the type III blue copper which exhibit complete diamagnetism.³⁻⁷

In a recent publication⁸ describing template condensation reactions of 5,5,5-trifluoro-4-(trifluoromethyl)-4-hydroxy-2-pentanone (hexafluorodiacetone alcohol, HFDA) with a series of amino alcohols $\text{NH}_2(\text{CH}_2)_n\text{OH}$ ($n = 2-6$) on Cu^{2+} , it was reported that dinuclear complexes having a 1:1 metal:ligand ratio are formed when $n = 4, 3$, or **2**, shown as **1-3**, respectively. The complex with the smallest chelate ring, **3**, had



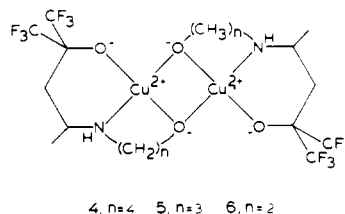
a normal magnetic moment, while the larger ring sizes of **1** and **2** led to a considerable decrease in magnetic moment, ascribed to antiferromagnetic coupling between adjacent copper(II) ions.

Current theories of coupling in complexes of this type suggest that exchange occurs via the bridging oxygen atoms.

The magnitude of the isotropic exchange parameter, $2J$, which describes this phenomenon, is critically dependent on subtle structural effects in the coordination geometry. In particular, Sinn and co-workers^{9,10} have demonstrated that distortion from planarity in the Cu_2O_2 bridging system markedly reduces $2J$. Such deviations from planarity may be described in terms of the distortion toward tetrahedral coordination at Cu (τ), the Cu-O-Cu angle at bridging oxygen (ϕ), and the distance (d_p) of the Cu atom above the basal plane of the four donor atoms.^{11,12}

In order to determine the values of these parameters in the two new complexes of reduced magnetic moment, we now report structure determinations on bis[μ -9,9,9-trifluoro-8-(trifluoromethyl)-6-methyl-5-azanon-5-ene-1,8-diolato(2-)- μ -O,N,O']-dicopper(II), $\text{Cu}_2\text{C}_{20}\text{H}_{26}\text{F}_{12}\text{N}_2\text{O}_4$ (**1**), and bis[μ -8,8,8-trifluoro-7-(trifluoromethyl)-5-methyl-4-azaoct-4-ene-1,7-diolato(2-)- μ -O,N,O']-dicopper(II), $\text{Cu}_2\text{C}_{18}\text{H}_{22}\text{F}_{12}\text{N}_2\text{O}_4$ (**2**).

Hydrogenation of the C-N double bonds¹³ in complexes **1-3** yields complexes **4-6**, respectively.⁸ The magnetic moments



in complexes **4-6** decrease as the chelate ring size increases.⁸ Work is currently in progress to establish what effect reduction of the C-N double bond has on the geometry in these complexes.

Comparisons of structural and magnetic data with a number of previously characterized compounds are made.

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Experimental Section

Preparation of the Complexes. The complexes were prepared by published methods.⁸ Materials of the highest available purity were used. Single crystals of both copper(II) complexes investigated, suitable for diffraction studies, were grown slowly from ethanol/acetone solutions.

X-ray Data Collection. The crystal of compound **2** which was selected had a truncated prismatic geometry. The base was rectangular (0.32 × 0.34 mm). The rectangle at the apex (0.32 × 0.08 mm) was parallel to the base. The ⊥ distance between the apical and basal rectangle was 0.40 mm. Data were collected on a CAD-4 automated diffractometer. Unit cell dimensions were determined from a least-squares treatment of 25 reflections obtained at medium and high angles by using Mo Kα₁ radiation (λ = 0.709 30 Å) and a graphite monochromator: *a* = 9.144 (2) Å, *b* = 11.364 (3) Å, *c* = 12.008 (2) Å, β = 97.05 (1)°, *V* = 1238 (1) Å³, *Z* = 4. The space group was uniquely determined to be *P*2₁/*c* from the systematic absences *0k0* with *k* = 2*n* + 1 and *h0l* with *h* + *l* = 2*n* + 1. The calculated density is 1.84 g cm⁻³, and the observed density, determined by flotation in 1,2-dibromopropane/2-chloroethanol, was found to be 1.83 (1) g cm⁻³. Intensity data were collected by the θ-2θ scan method. Scanning speeds ranged from approximately 20°/min for the most intense reflections to approximately 2°/min for the weakest. The angular scan width was *A* = 0.347(tan θ_{λ_{α2}}), where θ_{λ_{α2}} is determined from

$$\theta_{\lambda_{\alpha 2}} = \theta_{\lambda_{\alpha 1}} + \frac{\lambda_{\alpha 2} - \lambda_{\alpha 1}}{\lambda_{\alpha}} \frac{360}{2\pi} \tan \theta_{\lambda_{\alpha 1}}$$

and *A* depends on the crystal mosaic spread and on the divergence of the primary beam. *A* for this structure was 0.70. The scan was extended on each of the peaks by 25% for background determination. Reflections were collected up to 2θ = 48°. Three standard reflections, scanned approximately every 150 reflections, were used to place the intensity data on a common scale; systematic variation in these standards was not observed. Reflection intensities were calculated from peak and background measurements as *I* = *S*(*C* - *RB*), where *S* = scan rate, *C* = total integrated peak count, *B* = total background count, and *R* = ratio of the scan time for the peak to the scan time for the background. The estimated error was calculated as σ(*I*) = [S²(*C* + *R*²*B*) + (*pI*)²]^{1/2}. The value of *p* was 0.05. Of 2173 reflections originally scanned, 1879 unique ones with *I* > 3σ(*I*) were used in the solution and refinement of the structure. The intensities and σ(*I*) values were corrected for Lorentz and polarization effects. Neutral atom scattering factors¹⁴ were used, and the metal atom was corrected for anomalous dispersion (both real and imaginary). No absorption correction was required (μ = 18.3 cm⁻¹).

The crystal selected for complex **1** was square tetragonal, about 0.29 × 0.29 × 0.21 mm. Cell dimensions were determined as previously stated were *a* = 12.486 (3) Å, *b* = 19.387 (4) Å, *c* = 10.754 (2) Å, α = β = γ = 90°, *V* = 2603 (2) Å³, and *Z* = 4. The space group was uniquely determined to be *P**bca* from the systematic absences *0kl*, *k* = 2*n* + 1, *h0l*, *l* = 2*n* + 1, and *hk0*, *h* = 2*n* + 1. The calculated and observed densities are 1.82 and 1.81 (1) g cm⁻³, respectively. Intensity data were collected as previously described with reflections collected out to 2θ = 54°. Of 3218 unique reflections originally scanned 1905 unique ones with *I* > 3σ(*I*) were used in the refinement. The absorption coefficient (μ) is 18.2 cm⁻¹.

Structure Solution and Refinement. Copper atom positions for each structure were determined by Patterson methods. The remaining nonhydrogen positions were determined by difference Fourier methods. Hydrogen positions were calculated from geometrical considerations after anisotropic refinement of the other atomic positions, with use of C-H distances of 0.950 Å. They were then included as fixed contributions in the final stages of refinement. Recalculation of the hydrogen positions followed by refinement was continued until no further improvement in the residual was achieved. *R* values were calculated as *R*_F = [Σ||*F*_o| - |*F*_c||] / Σ|*F*_o| and *R*_{wF} = [Σw(|*F*_o| - |*F*_c||)² / Σw|*F*_o|²]^{1/2}. Reflections were weighted as w = 1/σ²(*F*_o) = 4*F*_o² / [σ(*F*_o)²]², where σ(*F*_o)² = [σ²(*I*) + (*pI*)²] / *Lp*. The function minimized was Σw(|*F*_o| - |*F*_c||). Refinement of the data for complex **2** resulted in *R*_F = 0.039 and *R*_{wF} = 0.061. The estimated standard deviation of an observation of unit weight was 2.145. Complex **1** gave

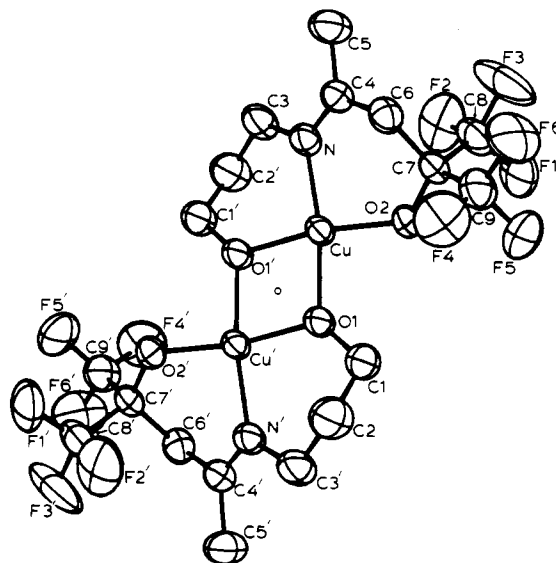


Figure 1.

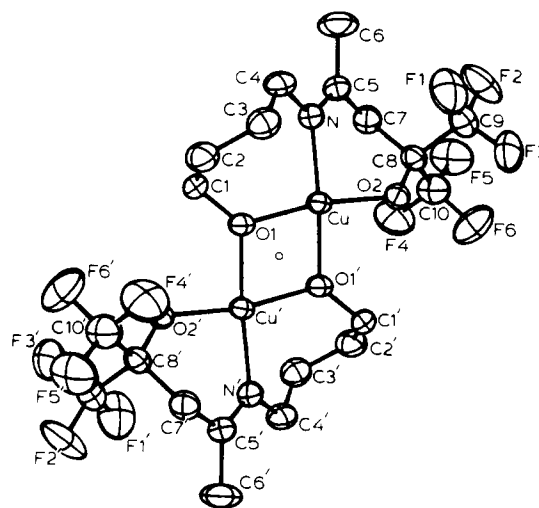


Figure 2.

*R*_F = 0.032 and *R*_{wF} = 0.045. The esd for an observation of unit weight was 1.343. Final difference Fourier maps were featureless.

Results and Discussion

Description of the Structures. Positional and thermal parameters for the two complexes are given in Tables I and II. The halves of each dinuclear complex are related by a center of symmetry. Cu-Cu distances are 2.995 (2) Å for compound **2** and 3.014 Å for compound **1**. Other distances and angles of interest are presented in Tables III and IV. Figures 1 and 2 present the complexes in views which facilitate comparison. Figures 3 and 4 illustrate the arrangement of the complexes in the unit cells. Thermal motion is moderate except for that of the fluorine atoms. There are apparently no H-bonding interactions between complexes.

Structural Comparisons. Since the two complexes **1** and **2** were already known to have similar magnetic properties, and considering that the ligands differed only by one methylene group, it was expected that the general coordination around Cu²⁺ in each would be similar. This proved to be the case, but the small differences observed are of some interest.

Both complexes were planar at the central CuO₁O_{1'}/Cu bridge, and in complex **1** the planarity extended across the coordination geometry of each Cu²⁺ ion (τ = 1.0°). With complex **2**, however, there was a small but significant tetrahedral distortion (τ = 6.8°).

(14) All calculations were performed on a PDP11 computer using programs from the Enraf-Nonius structure determination package (SDP), Enraf-Nonius, Delft, Holland, 1975; revised 1977.

Table I. Positional and Thermal Parameters and Their Estimated Standard Deviations in $\text{Cu}_2\text{C}_{18}\text{H}_{22}\text{F}_{12}\text{N}_2\text{O}_4^a$

| atom | x | y | z | B(1,1) | B(2,2) | B(3,3) | B(1,2) | B(1,3) | B(2,3) |
|------|-------------|--------------|-------------|-------------|-------------|-------------|--------------|--------------|-------------|
| Cu | 0.06769 (4) | -0.07404 (3) | 0.09593 (3) | 0.00866 (6) | 0.00598 (3) | 0.00506 (3) | -0.00157 (6) | -0.00190 (7) | 0.00263 (4) |
| F(1) | 0.2810 (4) | -0.0468 (3) | 0.4554 (2) | 0.0322 (6) | 0.0147 (2) | 0.0065 (2) | 0.0058 (7) | -0.0010 (6) | -0.0067 (3) |
| F(2) | 0.1368 (4) | -0.1812 (3) | 0.3954 (2) | 0.0329 (5) | 0.0228 (4) | 0.0085 (2) | -0.0200 (7) | 0.0191 (4) | -0.0028 (4) |
| F(3) | 0.3637 (5) | -0.2194 (3) | 0.4446 (2) | 0.0485 (8) | 0.0209 (3) | 0.0080 (2) | 0.0320 (8) | 0.0061 (7) | 0.0138 (4) |
| F(4) | 0.4844 (3) | -0.0481 (3) | 0.1677 (3) | 0.0171 (3) | 0.0178 (3) | 0.0151 (3) | -0.0089 (6) | 0.0130 (5) | 0.0048 (5) |
| F(5) | 0.4690 (3) | 0.0368 (3) | 0.3231 (3) | 0.0206 (4) | 0.0116 (2) | 0.0158 (3) | -0.0117 (6) | -0.0080 (6) | -0.0020 (4) |
| F(6) | 0.5628 (3) | -0.1352 (3) | 0.3192 (3) | 0.0117 (3) | 0.0160 (3) | 0.0249 (4) | 0.0022 (6) | -0.0132 (6) | 0.0090 (6) |
| O(1) | 0.0786 (3) | 0.0799 (2) | 0.0303 (2) | 0.0128 (3) | 0.0070 (2) | 0.0077 (2) | -0.0069 (4) | -0.0076 (4) | 0.0051 (3) |
| O(2) | 0.2020 (3) | -0.0388 (2) | 0.2224 (2) | 0.0103 (3) | 0.0066 (2) | 0.0062 (2) | 0.0019 (4) | -0.0040 (4) | 0.0004 (3) |
| N | 0.0421 (3) | -0.2397 (2) | 0.1388 (2) | 0.0106 (3) | 0.0072 (2) | 0.0059 (2) | -0.0042 (5) | -0.0005 (4) | 0.0034 (3) |
| C(1) | 0.1935 (5) | 0.1626 (4) | 0.0466 (4) | 0.0154 (5) | 0.0092 (3) | 0.0109 (3) | -0.0098 (7) | -0.0105 (7) | 0.0057 (6) |
| C(2) | 0.2171 (5) | 0.2233 (4) | -0.0560 (4) | 0.0130 (6) | 0.0117 (4) | 0.0133 (4) | -0.0085 (8) | -0.0041 (8) | 0.0065 (7) |
| C(3) | -0.1022 (5) | -0.2976 (4) | 0.1128 (3) | 0.0139 (5) | 0.0102 (3) | 0.0092 (3) | -0.0091 (7) | -0.0039 (7) | 0.0076 (5) |
| C(4) | 0.1502 (4) | -0.2972 (3) | 0.1892 (3) | 0.0131 (5) | 0.0065 (2) | 0.0054 (2) | 0.0001 (6) | 0.0015 (5) | 0.0015 (4) |
| C(5) | 0.1435 (5) | -0.4220 (3) | 0.2257 (4) | 0.0152 (6) | 0.0078 (3) | 0.0118 (4) | -0.0009 (7) | -0.0002 (9) | 0.0061 (5) |
| C(6) | 0.2982 (4) | -0.2382 (3) | 0.2102 (3) | 0.0105 (4) | 0.0078 (3) | 0.0062 (2) | 0.0039 (6) | 0.0013 (5) | -0.0005 (4) |
| C(7) | 0.2999 (4) | -0.1187 (3) | 0.2709 (3) | 0.0108 (4) | 0.0065 (2) | 0.0048 (2) | 0.0017 (6) | -0.0013 (5) | 0.0016 (4) |
| C(8) | 0.2711 (5) | -0.1405 (4) | 0.3919 (3) | 0.0200 (6) | 0.0106 (4) | 0.0052 (2) | 0.0057 (8) | 0.0005 (7) | 0.0032 (5) |
| C(9) | 0.4552 (5) | -0.0673 (3) | 0.2707 (4) | 0.0117 (6) | 0.0102 (4) | 0.0104 (4) | -0.0028 (7) | -0.0052 (8) | 0.0036 (6) |

| atom | x | y | z | B, Å ² | atom | x | y | z | B, Å ² |
|------|-------------|-------------|-------------|-------------------|-------|------------|-------------|------------|-------------------|
| H(1) | 0.2818 (0) | 0.1228 (0) | 0.0747 (0) | 3.5000 (0) | H(7) | 0.2375 (0) | -0.4455 (0) | 0.2613 (0) | 3.5000 (0) |
| H(2) | 0.1702 (0) | 0.2192 (0) | 0.0999 (0) | 3.5000 (0) | H(8) | 0.0728 (0) | -0.4295 (0) | 0.2770 (0) | 3.5000 (0) |
| H(3) | 0.2375 (0) | 0.1645 (0) | -0.1083 (0) | 3.5000 (0) | H(9) | 0.1160 (0) | -0.4706 (0) | 0.1622 (0) | 3.5000 (0) |
| H(4) | 0.3014 (0) | 0.2717 (0) | -0.0385 (0) | 3.5000 (0) | H(10) | 0.3330 (0) | -0.2260 (0) | 0.1397 (0) | 3.5000 (0) |
| H(5) | -0.0901 (0) | -0.3635 (0) | 0.0662 (0) | 3.5000 (0) | H(11) | 0.3634 (0) | -0.2897 (0) | 0.2545 (0) | 3.5000 (0) |
| H(6) | -0.1333 (0) | -0.3236 (0) | 0.1813 (0) | 3.5000 (0) | | | | | |

^a The form of the anisotropic thermal parameter is $\exp[-(B(1,1)h^2 + B(2,2)k^2 + B(3,3)l^2 + B(1,2)hk + B(1,3)hl + B(2,3)kl)]$.

Table II. Positional and Thermal Parameters and Their Estimated Standard Deviations in $\text{CH}_2\text{C}_{20}\text{H}_{26}\text{F}_{12}\text{N}_2\text{O}_4^a$

| atom | x | y | z | B(1,1) | B(2,2) | B(3,3) | B(1,2) | B(1,3) | B(2,3) |
|-------|-------------|-------------|-------------|-------------|--------------|-------------|-------------|-------------|-------------|
| Co | 0.41907 (3) | 0.53197 (2) | 0.08650 (3) | 0.00403 (2) | 0.00156 (1) | 0.00380 (3) | 0.00068 (3) | 0.00135 (5) | 0.00004 (3) |
| F(1) | 0.1450 (2) | 0.5864 (1) | 0.2295 (3) | 0.0063 (2) | 0.00404 (8) | 0.0200 (4) | -0.0019 (2) | 0.0044 (4) | 0.0055 (3) |
| F(2) | 0.1395 (2) | 0.6945 (1) | 0.2529 (3) | 0.0075 (2) | 0.00513 (8) | 0.0161 (3) | 0.0012 (2) | 0.0084 (4) | -0.0093 (2) |
| F(3) | 0.1017 (2) | 0.6497 (2) | 0.0789 (2) | 0.0053 (2) | 0.00571 (11) | 0.0133 (3) | 0.0020 (2) | -0.0041 (4) | -0.0015 (3) |
| F(4) | 0.4113 (2) | 0.7224 (1) | 0.0402 (3) | 0.0092 (2) | 0.00397 (8) | 0.0147 (3) | -0.0030 (2) | 0.0084 (4) | 0.0031 (3) |
| F(5) | 0.2864 (2) | 0.7718 (1) | 0.1397 (3) | 0.0150 (3) | 0.00177 (6) | 0.0140 (3) | 0.0010 (2) | 0.0058 (5) | -0.0012 (2) |
| F(6) | 0.2542 (2) | 0.7233 (1) | -0.0345 (2) | 0.0146 (3) | 0.00340 (8) | 0.0105 (2) | -0.0002 (3) | -0.0063 (4) | 0.0045 (2) |
| O(1) | 0.5351 (2) | 0.4687 (1) | 0.0843 (2) | 0.0057 (1) | 0.00236 (6) | 0.0041 (2) | 0.0027 (2) | 0.0026 (3) | 0.0013 (2) |
| O(2) | 0.3073 (2) | 0.5957 (1) | 0.0568 (2) | 0.0051 (1) | 0.00201 (6) | 0.0050 (2) | 0.0020 (2) | -0.0005 (3) | -0.0016 (2) |
| N | 0.3813 (2) | 0.5253 (1) | 0.2667 (2) | 0.0038 (1) | 0.00220 (7) | 0.0047 (2) | 0.0005 (2) | 0.0003 (3) | 0.0005 (2) |
| C(1) | 0.5701 (3) | 0.4263 (2) | 0.1828 (3) | 0.0050 (2) | 0.00290 (10) | 0.0045 (2) | 0.0026 (3) | 0.0009 (4) | 0.0019 (3) |
| C(2) | 0.4904 (3) | 0.3710 (2) | 0.2165 (3) | 0.0079 (3) | 0.00226 (9) | 0.0068 (3) | 0.0014 (3) | 0.0022 (6) | 0.0014 (3) |
| C(3) | 0.3778 (3) | 0.3975 (2) | 0.2438 (3) | 0.0061 (2) | 0.00228 (9) | 0.0071 (3) | -0.0008 (3) | 0.0006 (5) | 0.0011 (3) |
| C(4) | 0.3728 (3) | 0.4574 (2) | 0.3310 (3) | 0.0061 (2) | 0.00241 (9) | 0.0055 (3) | 0.0002 (3) | 0.0031 (5) | 0.0022 (3) |
| C(5) | 0.3538 (3) | 0.5797 (2) | 0.3231 (3) | 0.0048 (2) | 0.00247 (9) | 0.0045 (2) | 0.0008 (2) | -0.0004 (4) | -0.0008 (3) |
| C(6) | 0.3168 (4) | 0.5822 (2) | 0.4558 (4) | 0.0126 (4) | 0.00395 (14) | 0.0053 (3) | 0.0031 (4) | 0.0051 (6) | -0.0009 (4) |
| C(7) | 0.3576 (3) | 0.6471 (2) | 0.2550 (3) | 0.0055 (2) | 0.00191 (8) | 0.0063 (3) | 0.0003 (2) | -0.0006 (5) | -0.0020 (3) |
| C(8) | 0.2869 (3) | 0.6476 (2) | 0.1371 (3) | 0.0045 (2) | 0.00161 (7) | 0.0055 (2) | 0.0009 (2) | 0.0012 (4) | -0.0006 (3) |
| C(9) | 0.1676 (3) | 0.6453 (2) | 0.1742 (4) | 0.0050 (2) | 0.00237 (10) | 0.0091 (4) | 0.0008 (3) | 0.0010 (5) | -0.0014 (3) |
| C(10) | 0.3091 (3) | 0.7172 (2) | 0.0711 (4) | 0.0080 (3) | 0.00210 (9) | 0.0084 (4) | 0.0002 (3) | 0.0017 (6) | -0.0001 (3) |

| atom | x | y | z | B, Å ² | atom | x | y | z | B, Å ² |
|------|------------|------------|------------|-------------------|-------|------------|------------|------------|-------------------|
| H(1) | 0.5821 (0) | 0.4544 (0) | 0.2538 (0) | 4.0000 (0) | H(8) | 0.3065 (0) | 0.4558 (0) | 0.3744 (0) | 4.0000 (0) |
| H(2) | 0.6353 (0) | 0.4048 (0) | 0.1589 (0) | 4.0000 (0) | H(9) | 0.4469 (0) | 0.5196 (0) | 0.2848 (0) | 4.0000 (0) |
| H(3) | 0.5160 (0) | 0.3478 (0) | 0.2884 (0) | 4.0000 (0) | H(10) | 0.3005 (0) | 0.6285 (0) | 0.4777 (0) | 4.0000 (0) |
| H(4) | 0.4862 (0) | 0.3394 (0) | 0.1492 (0) | 4.0000 (0) | H(11) | 0.2546 (0) | 0.5544 (0) | 0.4649 (0) | 4.0000 (0) |
| H(5) | 0.3376 (0) | 0.3607 (0) | 0.2790 (0) | 4.0000 (0) | H(12) | 0.3719 (0) | 0.5652 (0) | 0.5083 (0) | 4.0000 (0) |
| H(6) | 0.3460 (0) | 0.4111 (0) | 0.1673 (0) | 4.0000 (0) | H(13) | 0.4296 (0) | 0.6559 (0) | 0.2313 (0) | 4.0000 (0) |
| H(7) | 0.4301 (0) | 0.4536 (0) | 0.3887 (0) | 4.0000 (0) | H(14) | 0.3336 (0) | 0.6825 (0) | 0.3094 (0) | 4.0000 (0) |

^a The form of the anisotropic thermal parameter is $\exp[-(B(1,1)h^2 + B(2,2)k^2 + B(3,3)l^2 + B(1,2)hk + B(1,3)hl + B(2,3)kl)]$.

The most interesting point of comparison between **1** and **2** is the chelate ring formed by the amino alcohol residue, which is seven membered in **1** and six membered in **2**; the former appears to be the first example of a dinuclear copper complex characterized with a seven-membered chelate ring in this position. Slight strain is evident in the six-membered ring in **2**, where the angle at C(2) is 120.1°, significantly greater than the tetrahedral angle, while the angles at C(1) and C(3) are respectively 112.7 and 114.7°. Because of the trigonal bonding of the nitrogen and oxygen atoms in these rings, little variation

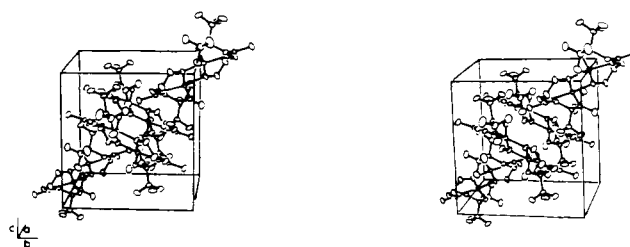
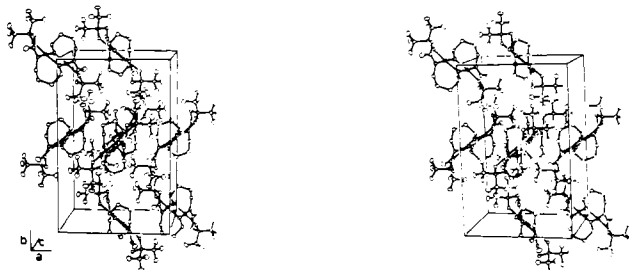


Figure 3.

Table III. Selected Bond Distances and Bond Angles for $\text{Cu}_2\text{C}_{18}\text{H}_{22}\text{F}_{12}\text{N}_2\text{O}_4$ (2)

| A. Bond Distances (Å) | | | |
|-----------------------|-----------|-----------|-----------|
| Cu-O(1') | 1.896 (2) | Cu-O(2) | 1.876 (2) |
| Cu-O(1) | 1.926 (2) | Cu-N | 1.973 (2) |
| O(1)'-C(1)' | 1.406 (3) | O(2)-C(7) | 1.355 (3) |
| N-C(3) | 1.473 (3) | N-C(4) | 1.274 (3) |
| C(1)'-C(2)' | 1.451 (5) | C(4)-C(6) | 1.504 (4) |
| C(2)'-C(3) | 1.451 (5) | C(6)-C(7) | 1.541 (3) |
| C(4)-C(5) | 1.487 (4) | C(7)-C(8) | 1.528 (3) |
| C(8)-F(1) | 1.306 (4) | C(7)-C(9) | 1.536 (4) |
| C(8)-F(2) | 1.318 (4) | C(9)-F(4) | 1.316 (4) |
| C(8)-F(3) | 1.338 (4) | C(9)-F(5) | 1.339 (4) |
| C(9)-F(6) | 1.327 (3) | | |

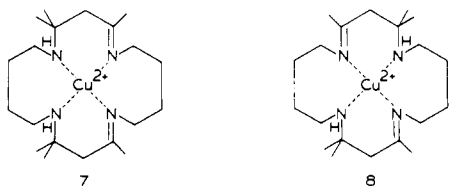
| B. Bond Angles (Deg) | | | |
|----------------------|------------|----------------|------------|
| O(1)-Cu-O(1)' | 76.80 (8) | N-Cu-O(1)' | 94.63 (7) |
| O(1)-Cu-O(2) | 94.33 (8) | N-Cu-O(2) | 94.55 (8) |
| O(1)'-Cu-O(2) | 169.33 (7) | O(1)-Cu-N | 170.74 (8) |
| Cu-O(1)-C(1)' | 128.7 (2) | Cu-O(2)-C(7) | 122.5 (2) |
| Cu-N-C(3) | 120.2 (2) | Cu-N-C(4) | 120.3 (2) |
| O(1)'-C(1)'-C(2)' | 112.7 (3) | O(2)-C(7)-C(8) | 109.6 (2) |
| C(1)'-C(2)'-C(3) | 120.1 (4) | O(2)-C(7)-C(9) | 107.8 (2) |
| C(2)'-C(3)-N | 114.7 (3) | O(2)-C(7)-C(6) | 114.8 (2) |
| C(3)-N-C(4) | 119.5 (2) | C(4)-C(6)-C(7) | 115.4 (2) |
| N-C(4)-C(5) | 124.9 (3) | C(5)-C(4)-C(6) | 116.4 (2) |
| N-C(4)-C(6) | 118.7 (2) | C(8)-C(7)-C(9) | 109.3 (2) |
| C(6)-C(7)-C(8) | 108.4 (2) | C(6)-C(7)-C(9) | 106.8 (2) |
| C(7)-C(8)-F(1) | 114.6 (3) | C(7)-C(9)-F(4) | 111.1 (3) |
| C(7)-C(8)-F(2) | 110.9 (2) | C(7)-C(9)-F(5) | 111.7 (3) |
| C(7)-C(8)-F(3) | 112.7 (3) | C(7)-C(9)-F(6) | 114.5 (2) |
| F(1)-C(8)-F(2) | 105.4 (3) | F(4)-C(9)-F(5) | 106.1 (3) |
| F(1)-C(8)-F(3) | 106.0 (3) | F(4)-C(9)-F(6) | 106.5 (3) |
| F(2)-C(8)-F(3) | 106.7 (3) | F(5)-C(9)-F(6) | 106.6 (3) |

**Figure 4.**

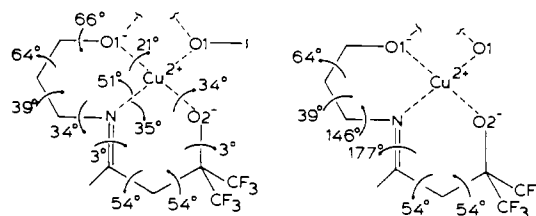
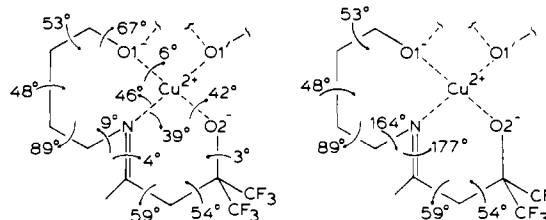
is possible in the position of the carbon atoms attached to them, and any strain in the carbon-chain "bridge" must therefore be largely taken up at the central carbon atom, C(2).

In compound 1, by contrast, there is no evidence of strain in the carbon chain in the seven-membered ring, where the angles at the four carbon atoms are all between 113 and 115°. From the six-membered to the seven-membered ring, there is virtually no change in the angle at oxygen or nitrogen, while the N-Cu-O "bite" angle increases from 94.6 to 98.7° in the larger ring. The slight distortion toward tetrahedral geometry at Cu^{2+} in 2 could be associated with the strain in the six-membered ring, but the effect is small and may be due solely to crystal packing forces.

A comparison of conformations of seven-membered chelate rings on Cu^{2+} may be made between 1 and the complex cations 7, $[\text{Cu}(\text{cis}-[18]\text{dieneN}_4)]^{2+}$, and 8, $[\text{Cu}(\text{trans}-[18]\text{dieneN}_4)]^{2+}$,

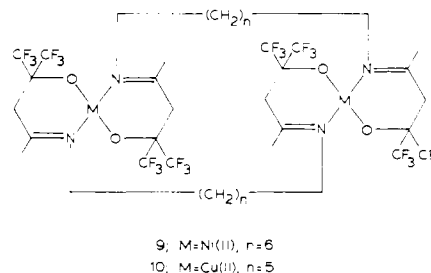


in which the metal is surrounded by tetraaza macrocyclic ligands.¹⁵ In the cis complex, 7, the tetrahedral distortion

**Figure 5.****Figure 6.**

reaches the large value of $\tau = 36.6^\circ$, so that the Cu^{2+} can hardly be described as being in square-planar coordination.¹⁶ This is attributed to the presence of a C_4 chain between donor imino groups within the macrocycle; examination of models shows that this cannot be accommodated without a twist of the ring. In the trans complex, 8, where the C_4 chain is between imino- and amino-donor groups, the distortion is considerably less ($\tau = 10.0^\circ$). In comparison with compound 1 in the present study, the strain-induced distortions of 7 and 8 would be expected to be more evident because of the cumulative effect of the macrocyclic system.

A six-membered β -imino fluorinated alkoxy ring is common to both 1 and 2. Its conformation is in each case the "half-boat" which has also been found in the $\text{Cu}(\text{II})$ complex 9 and its $\text{Cu}(\text{II})$ analogue 10.¹⁷ The torsional strain in this ring



appears to be less in 1 and 2, however, since the N-C-C-O atoms lie on well-defined planes (see Tables V and VI) as observed by Hodgson et al.¹⁸ for 6-membered "boats" in a number of copper(II) Schiff base complexes. This is not the case in 9 and 10.

Torsional strain within the other six-membered ring in compound 2 is concentrated about the C(1)' and C(2)'-C(3) bonds (Figures 1 and 5), with the ring in a twisted-chair conformation. Torsional strain in the 7-membered ring of compound 1 is apparent around the C(3)-C(4) and, to a lesser extent, the C(2)-C(3) bonds (Figures 2 and 6), and the ring is in a "folded under" conformation¹⁵ similar to that observed in 8.

It is clear that the difference in structural type and magnetic properties found between compounds 1 and 2 and those containing a 5-membered ring such as 3 is associated with the incompatibility of the shorter carbon chain with planar co-

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(16) Martin, J. W. L.; Payne, N. C.; Willis, C. J. *Inorg. Chem.* **1978**, *17*, 3478.

(17) Martin, J. W. L.; Payne, N. C.; Willis, C. J., unpublished results.

(18) Hodgson, D. J.; et al. *Inorg. Chem.* **1972**, *11*, 1826, 2216; **1973**, *12*, 1340, 2157, 2935; **1974**, *13*, 143, 1013; **1976**, *15*, 1712.

Table IV. Selected Bond Distances and Bond Angles for $\text{Cu}_2\text{C}_{20}\text{H}_{26}\text{F}_{12}\text{N}_2\text{O}_4$ (1)

| A. Bond Distances (Å) | | | |
|-----------------------|-----------|------------|-----------|
| Cu-O(1) | 1.898 (2) | Cu-O(2) | 1.892 (2) |
| Cu-O(1') | 1.924 (2) | Cu-N | 1.998 (2) |
| O(1)-C(1) | 1.410 (3) | O(2)-C(8) | 1.350 (3) |
| N-C(4) | 1.491 (4) | N-C(5) | 1.264 (4) |
| C(1)-C(2) | 1.506 (5) | C(5)-C(7) | 1.498 (4) |
| C(2)-C(3) | 1.526 (5) | C(7)-C(8) | 1.546 (4) |
| C(3)-C(4) | 1.493 (4) | C(8)-C(9) | 1.542 (4) |
| C(5)-C(6) | 1.501 (4) | C(8)-C(10) | 1.549 (4) |
| C(9)-F(1) | 1.318 (4) | C(10)-F(4) | 1.323 (4) |
| C(9)-F(2) | 1.322 (4) | C(10)-F(5) | 1.322 (4) |
| C(9)-F(3) | 1.317 (4) | C(10)-F(6) | 1.332 (4) |

| B. Bond Angles (Deg) | | | |
|----------------------|-----------|-----------------|------------|
| O(1)-Cu-O(1') | 75.94 (9) | N-Cu-O(1) | 98.65 (9) |
| O(1)-Cu-O(2) | 93.59 (8) | N-Cu-O(1') | 174.55 (9) |
| O(2)-Cu-N | 91.81 (9) | O(1)-Cu-O(2) | 169.50 (8) |
| Cu-O(1)-C(1) | 127.2 (2) | Cu-O(2)-C(8) | 121.2 (2) |
| Cu-N-C(4) | 121.6 (2) | Cu-N-C(5) | 118.4 (2) |
| O(1)-C(1)-C(2) | 113.0 (3) | O(2)-C(8)-C(9) | 109.1 (2) |
| C(1)-C(2)-C(3) | 114.6 (3) | O(2)-C(8)-C(10) | 108.8 (3) |
| C(2)-C(3)-C(4) | 114.9 (3) | O(2)-C(8)-C(7) | 114.4 (2) |
| C(3)-C(4)-N | 113.1 (3) | C(9)-C(8)-C(10) | 108.4 (3) |
| C(4)-N-C(5) | 119.6 (3) | C(7)-C(8)-C(9) | 109.8 (3) |
| N-C(5)-C(6) | 124.5 (3) | C(7)-C(8)-C(10) | 106.2 (3) |
| N-C(5)-C(7) | 119.0 (3) | C(5)-C(7)-C(8) | 112.8 (2) |
| F(1)-C(9)-F(2) | 106.2 (3) | F(4)-C(10)-F(5) | 106.5 (3) |
| F(1)-C(9)-F(3) | 105.8 (3) | F(4)-C(10)-F(6) | 106.0 (3) |
| F(1)-C(9)-C(8) | 110.4 (3) | F(4)-C(10)-C(8) | 110.8 (3) |
| F(2)-C(9)-F(3) | 106.6 (3) | F(5)-C(10)-F(6) | 107.2 (3) |
| F(2)-C(9)-C(8) | 113.7 (3) | F(5)-C(10)-C(8) | 113.8 (3) |
| F(3)-C(9)-C(8) | 113.6 (3) | F(6)-C(10)-C(8) | 112.1 (3) |

Table V. Least-Squares Planes through Selected Atoms and Deviations of Atoms from the Planes for $\text{Cu}_2\text{C}_{18}\text{H}_{22}\text{F}_{12}\text{N}_2\text{O}_4$ (2)

| (a) Deviations (Å) from the Planes (Planes Calculated by Using the Italicized Atoms) ^a | | | | | |
|--|---|--|--|--|--|
| plane 1 | <i>O</i> 1 (0.079), <i>N</i> (0.065), <i>O</i> 2 (-0.066), <i>O</i> 1' (-0.078), <i>Cu</i> (0.017) | | | | |
| plane 2 | <i>Cu</i> (0.000), <i>O</i> 1 (0.000), <i>Cu</i> ' (0.000), <i>O</i> 1' (0.000), <i>C</i> 1 (0.351) | | | | |
| plane 3 | <i>Cu</i> (0.000), <i>O</i> 1 (0.000), <i>O</i> 1' (0.000) | | | | |
| plane 4 | <i>Cu</i> (0.000), <i>N</i> (0.000), <i>O</i> 2 (0.000) | | | | |
| plane 5 | <i>N</i> (-0.010), <i>C</i> 4 (0.011), <i>C</i> 7 (-0.010), <i>O</i> 2 (0.009), <i>Cu</i> (0.627), <i>C</i> 6 (0.588) | | | | |

| (b) Equations of the Planes ^b | | | | | |
|--|--------|---------|---------|---------|----------------|
| plane | A | B | C | D | X ² |
| 1 | 0.7955 | -0.2928 | -0.5304 | 0.0031 | 2117 |
| 2 | 0.7550 | -0.3363 | -0.5629 | -0.0002 | 0 |
| 3 | 0.7550 | -0.3362 | -0.5630 | -0.0003 | |
| 4 | 0.8246 | -0.2656 | -0.4995 | 0.0461 | |
| 5 | 0.5777 | 0.0259 | -0.8158 | -1.3053 | 50 |

(c) Dihedral Angle between Planes 3 and 4: 6.8°

^a All atoms were weighted equally. The number in parentheses is the distance (Å) of the atom from the plane. Esd's of these distances are approximately 0.003 Å. ^b The equation of the plane is of the form $Ax + By + Cz - D = 0$.

ordination around oxygen. Instead, there is rehybridization of the bridging oxygen atoms from sp^2 to sp^3 as the ring bends. At the same time, association between dinuclear units occurs as an additional bond forms by coordination with the bridging oxygen atom in one unit to Cu^{2+} in a neighboring unit.

This association into tetranuclear units with a Cu_4O_4 "cubane" core has been well documented by other workers,¹⁹⁻²¹ and structural studies on **3** are now in progress to confirm its occurrence in the present system; it is already suspected be-

Table VI. Least-Squares Planes through Selected Atoms and Deviations of Atoms from the Planes for $\text{Cu}_2\text{C}_{20}\text{H}_{26}\text{F}_{12}\text{N}_2\text{O}_4$ (1)

| (a) Deviations (Å) from the Planes (Planes Calculated by Using the Italicized Atoms) ^a | | | | | |
|--|---|--|--|--|--|
| plane 1 | <i>O</i> 1 (0.001), <i>N</i> (-0.001), <i>O</i> 2 (0.001), <i>O</i> 1' (-0.001), <i>Cu</i> (-0.013) | | | | |
| plane 2 | <i>Cu</i> (0.000), <i>O</i> 1 (0.000), <i>Cu</i> ' (0.000), <i>O</i> 1' (0.000), <i>N</i> (0.023), <i>O</i> 2 (0.026), <i>C</i> 1 (0.131) | | | | |
| plane 3 | <i>Cu</i> (0.000), <i>O</i> 1 (0.000), <i>O</i> 1' (0.000) | | | | |
| plane 4 | <i>Cu</i> (0.000), <i>N</i> (0.000), <i>O</i> 2 (0.000) | | | | |
| plane 5 | <i>N</i> (0.006), <i>C</i> 5 (-0.007), <i>C</i> 8 (0.006), <i>O</i> 2 (-0.006), <i>Cu</i> (0.770), <i>C</i> 7 (0.628) | | | | |

| (b) Equations of the Planes ^b | | | | | |
|--|---------|---------|---------|----------|----------------|
| plane | A | B | C | D | X ² |
| 1 | -0.6300 | -0.7512 | -0.1972 | -11.2139 | 1 |
| 2 | -0.6361 | -0.7471 | -0.1928 | -11.2130 | 0 |
| 3 | -0.6361 | -0.7471 | -0.1929 | -11.2131 | |
| 4 | -0.6230 | -0.7557 | -0.2019 | -11.2415 | |
| 5 | 0.9173 | 0.3704 | -0.1463 | 7.7134 | 21 |

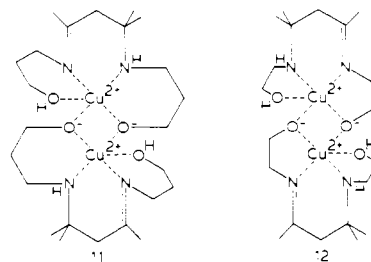
(c) Dihedral Angle between Planes 3 and 4: 1.0°

^a All atoms were weighted equally. The number in parentheses is the distance (Å) of the atom from the plane. Esd's of these distances are approximately 0.003 Å. ^b The equation of the plane is of the form $Ax + By + Cz - D = 0$.

cause of the normal magnetic moment of **3** which is characteristic of such a structure.

Magnetic Properties. A high degree of antiferromagnetic exchange is evident in both dinuclear complexes **1** and **2** with resultant reduced magnetic moments of 0.39 and 0.57 μ_B , respectively, at room temperature.⁸

Earlier studies on salicylaldiminato complexes¹¹ have shown that the tetrahedral distortion about the copper(II) ion (τ) in these four-coordinate dinuclear compounds should be small for effective spin pairing to occur. This requirement appears to be unimportant in five-coordinate copper(II) complexes, where the distortion (τ) of a basal plane in the approximately square-pyramidal cations bis[μ -5,7,7-trimethyl-4,8-diazaundec-4-ene-1,11-diolato(1-)- μ -*O,N,N',O'*]-dicopper(II)³ (**11**) and bis[μ -4,6,6-trimethyl-3,7-diazanon-3-ene-1,9-diolato(1-)- μ -*O,N,N',O'*]-dicopper(II)²² (**12**) is as high as 18.7 and



20.4°, respectively,³ and where the magnetic moment of the perchlorate salt of **12** is normal whereas that of the perchlorate salt of **11** is zero (diamagnetic at room temperature). The requirement is essentially satisfied in both complexes **1** and **2**, with complex **1** exhibiting almost perfect planarity ($\tau = 1.0^\circ$).

Another parameter used to relate structure to magnetic properties has been the angle at the bridging oxygen atoms (ϕ). Hodgson et al.^{12,13} have established a linear correlation between $2J$, the singlet-triplet splitting, and the ϕ angle in a series of hydroxo-bridged copper(II) dimers, but no such linearity is observed when an alkoxide oxygen, which is part of a chelate ring, is the bridging atom.²⁴ This lack of conformity

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Table VII. Some Magnetic and Structural Features

| complex | Cu-Cu, Å | $\phi(\text{Cu-O-Cu})$, deg | τ , deg | $2J$, cm^{-1} b |
|--|-------------|---------------------------------|-----------------|------------------------------|
| $[\text{Cu}(\text{5-Cl-salpn})]_2$ ^{a,c} | 2.92 | 103.7 | 13.7 | ≥ 800 |
| $[\text{Cu}(\text{3-NO}_2\text{-salpn})]_2$ ^{a,c} | 3.01 | 103.5 | 9.6 | ≥ 800 |
| $[\text{Cu}(\text{5,6-benz-o-salpn})]_2$ ^{a,c} | 3.04 | 104.0 | 10.4 | ≥ 800 |
| $[\text{Cu}(\text{5-NO}_2\text{-salpn})]_2$ ^{a,c} | 2.96 | 106.0 | 4.0 | ≥ 1000 |
| 2 ^e | 3.00 | 103.2 | 6.8 | ≥ 600 |
| 3 ^e | 3.01 | 104.1 | 1.0 | ≥ 600 |

^a salpn = salicylaldehyde 3-aminopropanol Schiff base.

^b Because of the very low observed paramagnetism (no maximum in the magnetic susceptibility vs. temperature curve at accessible temperatures), the values of $2J$ cannot be estimated accurately, though lower limits are clearly implied. ^c Reference 23.

^d Reference 24. ^e Reference 8 and this work.

in the alkoxy chelate series is probably due to the different strain effects produced by the wide variety of multidentate chelates employed in the comparison.

Table VII compares the various parameters of the complexes **1** and **2** with some other Cu(II) complexes of tridentate alkoxy ligands. There is obviously a general correlation between Cu-Cu distances, ϕ , τ , and $2J$ values, but no direct linear relationship is observed.

The effect of changing the chelate ring size from six to seven members on going from **2** to **1** is a barely significant decrease in the magnetic moment (from 0.57 to 0.38 μ_B at 300 K),

(24) Lemay, H. D.; Hodgson, D. J.; Pruetiangkura, P.; Theriot, L. J. *J. Chem. Soc., Dalton Trans.* 1979, 781.

consistent with the small changes in geometry around Cu^{2+} . In the absence of data on any other complex containing a 7-membered chelate ring in this position, it is difficult to suggest why compound **1** is not completely diamagnetic, since it appears to contain the ideal geometry ($\tau \approx 0^\circ$) for complete coupling.

The dramatic decrease in magnetic moment as the chelate ring containing the bridging oxygen atom increases from five to six members is consistent with previous observations¹⁹ and is associated with structural effects discussed above. As the bridging oxygen becomes trigonal, rather than tetrahedral, spin pairing between Cu^{2+} ions is facilitated because of more favorable orbital overlap.²⁵ Interactions between Cu^{2+} ions in complexes containing 5-membered chelate rings, where association into tetranuclear units may occur, are small but detectable, and we are currently undertaking a study on a group of such compounds in an attempt to elucidate further the relationship between structure and magnetic properties.

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Supplementary Material Available: Tables of calculated and observed structure factors for complex **1** (Table A) and complex **2** (Table B) (17 pages). Ordering information is given on any current masthead page.

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Crystal and Molecular Structure of Two Isomeric Iron Carbonyl Derivatives Which Contain an Extensively Rearranged Bis(tertiary phosphine)

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The bis(tertiary phosphines) $(\text{C}_6\text{H}_{11})_2\text{PC}=\overline{\text{CP}(\text{C}_6\text{H}_{11})_2(\text{CF}_2)_n}$ [A ($n = 2$), B ($n = 3$)] and $(\text{C}_6\text{H}_5)_2\text{PC}=\overline{\text{C}(\text{CF}_2)_2\text{C}=\overline{\text{C}(\text{C}_6\text{H}_5)_2(\text{CF}_2)_2}$ (C) react with iron carbonyls to give a number of products of known structure, namely, $(\text{L-L})\text{Fe}(\text{CO})_3$ [$(\text{L-L}) = A$ or B], $(\text{L-L})\text{Fe}_2(\text{CO})_6$ [$(\text{L-L}) = A$], and $(\text{L-L})\text{Fe}_2(\text{CO})_8$ [$(\text{L-L}) = C$]. In addition two isomers of formula $(\text{L-L})\text{Fe}_2(\text{CO})_6$ (V and VI) can be isolated from the reactions of C , and the structures of these were determined by conventional X-ray crystallographic techniques. The cell constants for V are $a = 15.348$ (6) Å, $b = 9.231$ (5) Å, $c = 26.839$ (12) Å, and $\beta = 104.90$ (3)°; the space group is $P2_1/c$. The cell constants for VI are $a = 12.45$ (2) Å, $b = 17.21$ (5) Å, $c = 18.86$ (3) Å, and $\beta = 97.67$ (9)°; the space group is $P2_1/c$. The structures of V and VI were refined by full-matrix least-squares techniques to conventional R indices of 0.055 and 0.072, respectively. In IV the basic structure consists of two $\text{Fe}(\text{CO})_3$ moieties bridged by two different phosphido groups. One of those groups is a $-\overline{\text{P}(\text{C}_6\text{H}_5)_2}$ unit which has been cleaved from the ligand and the other is a $-\overline{\text{P}(\text{C}_6\text{H}_5)\text{C}=\overline{\text{C}(\text{CF}_2)_2\text{C}=\overline{\text{C}(\text{C}_6\text{H}_5)_2(\text{CF}_2)_2}}$ group formed by extensive rearrangement of the remainder of the ligand. The phenyl group migrates from the phosphorus to the end of the conjugated fluorocarbon chain. In VI , again two bridged $\text{Fe}(\text{CO})_3$ fragments are present. One of these is a cleaved $-\overline{\text{P}(\text{C}_6\text{H}_5)_2}$ group but the other is the intact remaining portion of the ligand which forms a metal-carbon σ bond to one iron atom and coordinates to the second iron with the remaining phosphorus atom. These unusual ligand fragmentation reactions are discussed in the light of related examples.

Introduction

The reactions of bis(tertiary phosphines and arsines) with metal carbonyls usually result in simple substitution of carbonyl groups.¹ In our laboratories we are currently interested

in the properties of the fluorocarbon-bridged ligands A , B , and C , which belong to a class of compounds which have unsaturated bridging groups. In principle they could use the unsaturated bridge in bonding,²⁻⁷ but in practice ligands related

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