

The pentacoordinate Ni case is presented on the right side of Figure 5. The fact that one of the equatorial ammonia ligands becomes noncoplanar, together with the absence of one axial ligand, makes the two Ni magnetic orbitals closer in energy, with the  $d_{z^2}$  combination below the  $d_{xy}$  one. This latter combination interacts strongly with the  $n_2$  orbital of the bridging oxamidato, making up the SOMO  $\varphi_2'$ . The  $d_{z^2}$  magnetic orbital remains lower and well separated in energy ( $\varphi_3'$ ) according to the classical pentacoordination scheme.

If we consider the antiferromagnetic part of the doublet-quartet gap, related to the mono-electronic promotion energy of one electron placed in  $\varphi_3$  ( $\varphi_3'$ ) to  $\varphi_1$  ( $\varphi_1'$ ), it is easy to realize that the pentacoordinated dinuclear complex should have a stronger antiferromagnetic coupling constant than the hexacoordinate complex.

It is worth noting that, in the absence of correlation and polyelectronic corrections, the electronic doublet constituted mainly by the SOMO, which contains the unpaired electron, has a strong Ni  $d_{z^2}$  character (83%) in the hexacoordinate dinuclear Ni com-

plex, while it is Ni  $d_{xy}$  (68%) in the pentacoordinate complex.

**Acknowledgment.** We are very grateful for the financial assistance from the CICYT (Grant No. MAT88-0545). We thank Andrea Dei (Dipartimento di Chimica, Università di Firenze), for helpful suggestions and stimulating discussions.

**Registry No.** 1, 141090-75-7; 2, 141090-79-1; 3, 141090-77-9; 4, 141090-81-5; 5, 141090-85-9; 6, 141090-83-7; 7, 141090-88-2; [Cu(oxpn)], 20102-49-2; [Cu(Me<sub>2</sub>oxpn)], 21780-20-1; [Cu(OHoxpn)], 141090-86-0; [Ni(*d,l*-cth)](ClO<sub>4</sub>)<sub>2</sub>, 15392-95-7; [Ni<sub>2</sub>(OH)<sub>2</sub>(Me<sub>3</sub>-[12]N<sub>3</sub>)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>, 66756-81-8; [Ni<sub>2</sub>(OH)<sub>2</sub>(Me<sub>4</sub>[12]N<sub>3</sub>)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>, 74911-34-5.

**Supplementary Material Available:** Text giving experimental details of the structure determination for 1 and 5 and tables of complete crystallographic data for 1 and 5, bond distances and angles for 1 and 5, anisotropic thermal parameters for 1 and 5, and hydrogen atom coordinates for 1 (10 pages); tables of calculated and observed structure factors (17 pages). Ordering information is given on any current masthead page.

Contribution from SFA Inc., Landover, Maryland 20785, the Chemistry Division, Code 6120, and Laboratory for the Structure of Matter, Code 6030, Naval Research Laboratory, Washington, D.C. 20375-5000, and the Department of Chemistry, Catholic University, Washington, D.C. 20064

## Synthesis, Structure, and Magnetic Properties of Cu<sub>4</sub>(μ-OCMe<sub>3</sub>)<sub>6</sub>[OC(CF<sub>3</sub>)<sub>3</sub>]<sub>2</sub> and Cu<sub>3</sub>(μ-OCMe<sub>3</sub>)<sub>4</sub>[OC(CF<sub>3</sub>)<sub>3</sub>]<sub>2</sub>

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Received October 10, 1991

The reaction of a moderate excess of perfluoro-*tert*-butyl alcohol (H[PFTB]) with [Cu(OCMe<sub>3</sub>)<sub>2</sub>]<sub>*n*</sub> in hydrocarbon solvents affords two primary products, Cu<sub>4</sub>(μ-OCMe<sub>3</sub>)<sub>6</sub>[PFTB]<sub>2</sub> (1) and Cu<sub>3</sub>(μ-OCMe<sub>3</sub>)<sub>4</sub>[PFTB]<sub>2</sub> (2), with their relative amounts determined by the reaction stoichiometry. Compound 1 is purified by recrystallization, and 2 is isolated by sublimation of a mixture of 1 and 2. Both compounds have well-resolved NMR spectra ( $\nu_{1/2}$  = 45–90 Hz) and no X-band ESR spectra, indicative of a short electron relaxation time. Compound 1 crystallizes in space group  $P\bar{1}$  [ $f_w$  = 1162.9,  $a$  = 10.609 (3) Å,  $b$  = 10.667 (3) Å,  $c$  = 11.151 (3) Å,  $\alpha$  = 100.69 (3)°,  $\beta$  = 95.37 (3)°,  $\gamma$  = 99.65 (3)°,  $V$  = 1212.3 (7) Å<sup>3</sup>,  $Z$  = 1 (two half-molecules),  $d_{\text{calcd}}$  = 1.593 g/cm<sup>3</sup>,  $F(000)$  = 588,  $\mu$  = 18.43 cm<sup>-1</sup>,  $T$  = 295 K]. It consists of three Cu<sub>2</sub>O<sub>2</sub> linked twisted rings with bridging OCMe<sub>3</sub> groups and two terminal PFTB groups, where the central Cu atoms are 4-coordinate and the two outer Cu atoms are 3-coordinate. The {CuO<sub>3</sub>} moieties are Y-shaped and planar [terminal Cu–O = 1.797 (5) Å, bridging 3-coordinate Cu–O = 1.856 (4) and 1.865 (4) Å, and bridging 4-coordinate Cu–O = 1.947 Å (average)]. Magnetic measurements (77–300 K) show both 1 and 2 to be antiferromagnetically coupled. The magnetic data for 1 fit a theoretical equation for a linear centrosymmetric tetranuclear d<sup>9</sup> system [ $J$  = -131.6 (0.6) cm<sup>-1</sup>], and the data for 2 fit the corresponding trinuclear equation [ $J$  = -114.4 (1.5) cm<sup>-1</sup>].

Copper(II) alkoxide chemistry has advanced considerably in the last decade, in part due to the discovery of cuprate superconductors and the resulting search for new molecular precursors.<sup>2</sup> As fluorinated alkoxides are often much more volatile than their hydrocarbon counterparts,<sup>3</sup> we sought to prepare fluorinated copper(II) alkoxides by two distinct routes. Metathesis/salt elimination, a standard preparative method for alkoxides, allowed the synthesis of the first crystallographically characterized 3-coordinate Cu(II) complex, Ba[Cu[OCMe(CF<sub>3</sub>)<sub>2</sub>]<sub>2</sub>]<sub>2</sub>, as well as

a highly volatile compound which was tentatively identified as Cu<sub>4</sub>[OC(CF<sub>3</sub>)<sub>3</sub>]<sub>7</sub>.<sup>4</sup> Alcohol-interchange reactions (eqs 1 and 2)



are another common synthetic method for metal alkoxides<sup>5</sup> and have been used for Cu(II) systems.<sup>2a-c</sup> Replacement of the OR groups by OR' is often incomplete (eq 2) when bulky alkoxides and/or alcohols are involved or when the starting alkoxide has both strongly bound bridging and more easily replaced terminal alkoxy groups.<sup>2b,5</sup> Also, recent work has shown that approximately 50% substitution of *tert*-butoxy groups occurred in reactions between copper(I) *tert*-butoxide [(CuOCMe<sub>3</sub>)<sub>4</sub>] and various fluorinated alcohols.<sup>6</sup> In our study of alcoholysis reactions between [Cu(OCMe<sub>3</sub>)<sub>2</sub>]<sub>*n*</sub> and two common fluorinated alcohols, (F<sub>3</sub>C)<sub>3</sub>-COH (H[PFTB]) and Me(F<sub>3</sub>C)<sub>2</sub>COH (H[HFTB]), partial replacement of the *tert*-butoxide ligands occurred. This paper includes an account of those alcoholysis reactions, a crystallo-

(1) SFA Inc. Currently at NRL, Code 6120.

(2) (a) Goel, S. C.; Kramer, K. S.; Gibbons, P. C.; Buhro, W. E. *Inorg. Chem.* 1989, 28, 3620–3622. (b) Horowitz, H. S.; McLain, S. J.; Sleight, A. W.; Drulinger, J. D.; Gai, P. L.; Vanhavelaar, M. J.; Wagner, J. L.; Biggs, B. D.; Poon, J. J. *Science* 1989, 243, 66–69. (c) Goel, S. C.; Kramer, K. S.; Chaing, M. Y.; Buhro, W. E. *Polyhedron* 1990, 9, 611. (d) McMullen, A. K.; Tilley, T. D.; Rheingold, A. L.; Geib, S. J. *Inorg. Chem.* 1989, 28, 3772. (e) Sauer, N. N.; Garcia, E.; Salazar, K. V.; Ryan, R. R.; Martin, J. A. *J. Am. Chem. Soc.* 1990, 112, 1524. (f) Rupich, M. W.; Lagos, B.; Hackey, J. P. *Appl. Phys. Lett.* 1989, 55, 2447–2449. (g) Caulton, K. G.; Hubert-Pfalzgraf, L. G. *Chem. Rev.* 1990, 90, 969. (h) Singh, J. V.; Baranwal, B. P.; Mehrotra, R. C. *Z. Anorg. Allg. Chem.* 1981, 477, 235–240. (i) Banait, J. S.; Pahil, P. K. *Synth. React. Inorg. Met.-Org. Chem.* 1988, 18, 309–315. (j) Purdy, A. P.; George, C. F.; Callahan, J. H. *Inorg. Chem.* 1991, 30, 2812–2819.

(3) Willis, C. J. *Coord. Chem. Rev.* 1988, 88, 133–202.

(4) Purdy, A. P.; George, C. F. *Inorg. Chem.* 1991, 30, 1969–1970.

(5) Bradley, D. C.; Mehrotra, R. C.; Gaur, D. P. *Metal Alkoxides*; Academic Press: London, 1978.

(6) Gross, M. E. *J. Electrochem. Soc.* 1991, 138, 2422–2426.

graphic study, and magnetic measurements on some of the products.

### Experimental Section

All manipulations were conducted either on the vacuum line or under helium in a Vacuum Atmospheres Dri-Lab, and all reactions were performed in Pyrex bulbs equipped with a stir-bar and a Kontes Teflon valve. H[PFTB] was obtained from PCR and was transferred to the reaction bulbs on the vacuum line.  $[\text{Cu}(\text{OCMe}_3)_2]_n$  was obtained from a reaction between  $(\text{CuOCMe}_3)_4$  and  $(\text{Me}_3\text{CO})_2$ .<sup>7</sup> All NMR tubes were sealed under vacuum. NMR spectra were recorded on a Bruker MSL-300 spectrometer, and residual protons (of  $\text{C}_6\text{D}_6$ ,  $^1\text{H}$ ) and added  $\text{CFCl}_3$  ( $^{19}\text{F}$ ) were used as chemical shift references. Melting points were determined in sealed capillaries under 1 atm of He. All sublimations were performed under dynamic vacuum. Electronic spectra were recorded on a Cary 2390 spectrometer, and IR spectra were obtained on a Perkin-Elmer 1430 ratio recording spectrometer using mineral oil mulls between KBr plates. ESR spectra were recorded on  $\text{C}_6\text{H}_6$  solutions with a Varian X-band instrument, at room temperature and at  $-196^\circ\text{C}$ . Powder diffraction measurements used a Phillips diffractometer with a graphite crystal monochromator and  $\lambda = 1.54050 \text{ \AA}$ . Elemental analyses were obtained from E+R Microanalytical Laboratories, Corona, NY.

**Synthesis of  $\text{Cu}_4(\mu\text{-OCMe}_3)_4(\text{PFTB})_2$  (1).** A mixture of H[PFTB] (0.38 g, 1.6 mmol),  $[\text{Cu}(\text{OCMe}_3)_2]_n$  (0.43 g, 2.0 mmol), and 5:1 heptane/benzene (10 mL) was stirred for 8 h at  $70\text{--}75^\circ\text{C}$  and then for 1 d at room temperature. Solvents were removed in vacuo, and the residue was dissolved in  $\text{C}_6\text{H}_6$ . The mixture was filtered, and the filtrate was evaporated in vacuo. Recrystallization from heptane afforded  $\text{Cu}_4(\mu\text{-OCMe}_3)_4(\text{PFTB})_2$  (1) in 0.30-g yield (51%). Mp:  $155\text{--}173^\circ\text{C}$ . Anal. Calcd (found) for  $\text{C}_{32}\text{H}_{44}\text{F}_{18}\text{O}_8\text{Cu}_4$ : C, 33.05 (33.08); H, 4.68 (4.80); F, 29.41 (29.67); Cu, 21.86 (22.06). UV/vis, nm ( $\epsilon$ ): 315 (10500), 740 (450), 850 (240), 1000 (170). IR,  $\text{cm}^{-1}$ : 465 (w), 492 (w), 542 (vw), 620 (m), 655 (w), 730 (s), 765 (m), 777 (w), 905 (s), 973 (vs), 1177 (s), 1200 (s), 1212 (s), 1245 (s), 1265 (vs), 1302 (s).  $^1\text{H}$  NMR:  $\delta$  11.54 (36 H,  $\nu_{1/2} = 90 \text{ Hz}$ ), 14.61 (18 H,  $\nu_{1/2} = 70 \text{ Hz}$ ).  $^{19}\text{F}$  NMR:  $\delta$   $-62.27$  ( $\nu_{1/2} = 45 \text{ Hz}$ ). Concentration dependence at  $20^\circ\text{C}$  in  $\text{C}_6\text{D}_6$  (relative  $^1\text{H}$  integral for each species): for 0.00187 M, 1 (0.672), 2 (0.221), 4 (0.027),  $\text{Me}_3\text{COH}$  (0.08); for 0.00882 M, 1 (0.744), 2 (0.169), 4 (0.067),  $\text{Me}_3\text{COH}$  (0.02); for 0.0143 M, 1 (0.764), 2 (0.111), 4 (0.113),  $\text{Me}_3\text{COH}$  (0.01). Temperature dependence of a 0.00685 M solution in  $\text{C}_7\text{D}_8$  [ $T$ , K (fraction of total  $^{19}\text{F}$  integral for 1 at each temperature)]: 263 (63%), 273 (61%), 283 (60%), 293 (58%), 318 (53%), 335 (49%). At 253 K, additional broad peaks appear in the  $^{19}\text{F}$  spectrum at  $\delta$   $-58.3$ ,  $-74.6$ , and  $-61.8$  and in the  $^1\text{H}$  spectrum at  $\delta$  2.47. The relative  $^1\text{H}$  integral for 4 increases with temperature: 293 K (3%), 318 K (6%), 335 K (8%), 350 K (9%). 1 sublimed with decomposition at  $90\text{--}120^\circ\text{C}$ ; the sublimate was primarily 2 and showed evidence for a small amount of an unknown compound in the  $^{19}\text{F}$  spectrum ( $\delta$   $-49.83$ ). The sublimation residue was identified as  $[\text{Cu}(\text{OCMe}_3)_2]_n$  by its powder diffraction pattern [ $d$ ,  $\text{Å}$  ( $I/I_0$ ): 8.927 (76), 8.499 (100), 8.299 (72), 8.261 (73), 5.035 (7), 4.831 (5), 4.339 (9), 4.267 (9), 3.948 (7), 3.798 (16), 3.411 (7), 3.206 (15), 3.051 (11), 2.855 (9), 2.812 (10), 2.642 (9), 2.544 (11), 2.192 (5), 2.128 (2), 1.896 (5), 1.817 (4), 1.748 (1), 1.729 (1), 1.649 (2), 1.593 (2), 1.529 (2), 1.356 (1), 1.322 (1)].

A repeated preparation using a 5:2 mole ratio (0.75 mmol of  $[\text{Cu}(\text{OCMe}_3)_2]_n$  and 0.30 mmol of H[PFTB]) resulted in 0.22 mmol of  $[\text{Cu}(\text{OCMe}_3)_2]_n$  being unreacted. A 49% isolated yield of crystalline 1 was obtained.

**Synthesis of  $\text{Cu}_3(\mu\text{-OCMe}_3)_4(\text{PFTB})_2$  (2).**  $[\text{Cu}(\text{OCMe}_3)_2]_n$  (0.23 g, 1.1 mmol) and H[PFTB] (0.61 g, 2.6 mmol) were combined in heptane (15 mL), and the mixture was stirred for 18 h. A small quantity of solids remained. After brief warming with a heat gun, the solvents were removed, leaving  $\approx 0.25$  g of yellow product. An NMR spectrum showed the latter to be  $\approx 75\%$  2. Several attempts to crystallize 2 from benzene or heptane failed, as only 1 crystallized. Sublimation of a 129-mg portion at  $110^\circ\text{C}$  afforded 79 mg of 2 and a nonvolatile residue. Mp:  $115\text{--}118^\circ\text{C}$ . Anal. Calcd (found) for  $\text{C}_{24}\text{H}_{36}\text{O}_8\text{F}_{18}\text{Cu}_3$ : C, 30.24 (30.03); H, 3.81 (3.86); F, 35.88 (35.80); Cu, 19.99 (20.27). UV/vis, nm ( $\epsilon$ ): 320 (8900), 740 (340), 850 (200), 1000 (130). IR,  $\text{cm}^{-1}$ : 465 (w), 490 (w), 542 (w), 622 (w), 650 (m), 728 (s), 764 (m), 778 (w), 903 (m), 973 (vs), 1174 (s), 1198 (s), 1215 (s), 1243 (vs), 1270 (vs), 1302 (s).  $^1\text{H}$  NMR:  $\delta$  15.75 ( $\nu_{1/2} = 85 \text{ Hz}$ ).  $^{19}\text{F}$  NMR:  $\delta$   $-59.89$  ( $\nu_{1/2} = 55 \text{ Hz}$ ). About 5% 1 was present in solution according to the NMR spectra.

**Controlled Hydrolysis of 1.** Water (0.037 mmol) was condensed into a frozen solution of 1 (35 mg, 0.030 mmol) in  $\text{C}_6\text{H}_6$  (5 mL). The mixture was stirred at room temperature for 2.5 h and filtered. Solvent was removed from the filtrate in vacuo, affording a yellow-brown solid, which

was identified as primarily 2 by the NMR spectrum. An unidentified species with a peak at  $\delta(^{19}\text{F})$   $-53.4$  was also present. The black residue was amorphous by powder diffraction and not identified.

**Double Treatment of  $[\text{Cu}(\text{OCMe}_3)_2]_n$  with H[PFTB].** (a) A mixture of  $[\text{Cu}(\text{OCMe}_3)_2]_n$  (0.23 g, 1.1 mmol), H[PFTB] (0.35 g, 1.5 mmol), and heptane (5 mL) was stirred at  $60\text{--}80^\circ\text{C}$  for 3.5 h. After volatile materials were removed in vacuo, heptane and H[PFTB] (0.28 g) were added and the mixture was stirred at  $70^\circ\text{C}$  for 12 h, during which a thick brown material precipitated. After the volatile materials were removed, the residue was redissolved in heptane. The resulting mixture was filtered through dry talc, and the filtrate was evaporated, leaving 0.21 g of solid. A semiliquid orange-brown material sublimed at  $40\text{--}50^\circ\text{C}$  from the latter (NMR: large peak for 2 and broad humps at  $\delta$   $-67.6$  and  $-72.1$  in  $^{19}\text{F}$ ; mostly 2 in  $^1\text{H}$ ). The sublimation residue was identified as 2 by NMR spectroscopy.

(b) H[PFTB] (0.28 g, 1.2 mmol) was allowed to react with  $[\text{Cu}(\text{OCMe}_3)_2]_n$  (0.20 g, 0.96 mmol) in 5 mL of heptane at room temperature for 1 d. Volatile materials were removed, and residue was stirred with H[PFTB] (0.24 g, 1.0 mmol) in heptane (5 mL) for 4 d. After the solvent was evaporated, the residue was dissolved in heptane. The resulting mixture was filtered, and the volatile materials were removed to afford a yellow solid (0.27 g) that was coated with a green substance around the edges. Sublimation of a portion (0.16 g) of the yellow solid started about  $50^\circ\text{C}$  and continued to  $90^\circ\text{C}$ . The sublimate was collected in two portions. NMR spectra of the first portion showed 2 and unidentified, broad peaks at  $\delta(^{19}\text{F})$   $-52.8$ ,  $-50.3$ , and  $-42.5$  and at  $\delta(^1\text{H})$  21.9 and 20.7; NMR spectra of the second portion showed 2 with some 1.

**Synthesis of  $\{\text{Cu}(\text{OCMe}_3)_2\}_n\{\text{HFTB}\}_n$  (3).** H[HFTB] (0.5 mL, 4 mmol) was added to  $[\text{Cu}(\text{OCMe}_3)_2]_n$  (0.25 g, 1.2 mmol) in  $\approx 25$  mL of heptane, and the mixture was stirred for 4 d at ambient temperature. Volatile materials were removed in vacuo; then  $\text{C}_6\text{H}_6$  (25 mL) and another 0.5 mL of H[HFTB] were added, and the mixture was stirred for 5 d at  $70^\circ\text{C}$ . Following removal of volatile materials, the product was redissolved in  $\text{C}_6\text{H}_6$  and the mixture was filtered (0.075 g of residue on the frit). Evaporation of the filtrate afforded  $\{\text{Cu}(\text{OCMe}_3)_2\}_n\{\text{HFTB}\}_n$  (0.23 g, 61%), which was purified by recrystallization from heptane. Mp:  $157\text{--}165^\circ\text{C}$ . Anal. Calcd (found) for  $\text{C}_8\text{H}_{12}\text{F}_2\text{O}_2\text{Cu}$ : C, 30.24 (30.40); H, 3.81 (4.14); F, 35.88 (35.57); Cu, 20.00 (20.33). UV/vis, nm ( $\epsilon$ ): 270 (1400), 365 (3100), 725 (110), 825 (75), 980 (50).  $^1\text{H}$  NMR:  $\delta$  16.43 (21% H), 14.76 (7%), 14.21 (23%), 12.50 (7%), 11.52 (7%), 10.37 (17%),  $-0.70$  (17%).  $^{19}\text{F}$  NMR:  $\delta$   $-69.34$ ,  $-66.75$ ,  $-65.36$ ,  $-65$  (broad hump). The product sublimed  $110^\circ\text{C}$  with decomposition. The soluble part of sublimate showed NMR resonances identical to those of 3.

**X-ray Data Collection and Structure Refinement.** A green irregular ( $0.18 \times 0.43 \times 0.58 \text{ mm}$ ) crystal was mounted under He atmosphere in a thin-walled glass capillary for data collection on a Nicolet R3m/V automated four-circle diffractometer using an incident-beam monochromator. A total of 5904 reflections were measured in the  $\theta/2\theta$  mode to  $2\theta_{\text{max}} = 55^\circ$  ( $0 \leq h \leq 13$ ,  $-13 \leq k \leq 13$ ,  $-14 \leq l \leq 14$ ), of which 3485 were observed with  $F_o > 3\sigma(F)$  ( $R_{\text{merge}} = 0.031$ ). Corrections were applied for Lorentz and polarization effects. A semiempirical absorption correction based on the  $\varphi$  dependence of 12 reflections with  $\chi = \text{ca. } 90^\circ$  was applied, and maximum and minimum transmissions were 0.98 and 0.68, respectively. The structure was solved by direct methods with the aid of the program SHELEXTL<sup>8</sup> and refined with a full-matrix least-squares procedure<sup>9</sup> in which the function minimized was  $\sum w(|F_o| - |F_c|)^2$ . The 308 parameters refined included the coordinates and anisotropic thermal parameters for all non-hydrogen atoms. Hydrogens were included using a riding model in which the coordinate shifts of the carbons were applied to the attached hydrogens,  $\text{C-H} = 0.96 \text{ \AA}$ , and H angles were idealized. Each of the  $\text{CF}_3$  groups was disordered, and the fluorines were refined in two orientations with the occupancy required to sum to 1.0. The lower occupancy fluorines were refined with fixed isotropic thermal parameters. The goodness-of-fit parameter was 1.64. The final difference Fourier excursions were 0.71 and  $-0.50 \text{ e \AA}^{-3}$ . Structure solution and refinement were tested in P1 but resulted in poor bond distances and no improvement in  $R$  values.

**Magnetic Susceptibility Measurements.** The magnetic susceptibilities were measured between 80 and 300 K on a computer-controlled Faraday system which consists of a Cahn 2000 microbalance, Applied Magnetics electromagnet, Lake Shore Cryotronics temperature controller, platinum resistance thermometer, and Abbess instrument cryostat. A Data Translation A/D board and AT computer were used to monitor the microbalance output and temperature readings. The instrument was calibrated with  $\text{HgCo}(\text{NCS})_4$ .<sup>9</sup> Samples were placed in either gelatin

(7) Tsuda, T.; Hashimoto, T.; Saegusa, T. *J. Am. Chem. Soc.* 1972, 94, 658–659.

(8) Sheldrick, G. M. *SHELEXTL80 Minicomputer Programs for Structure Determination*; University of Göttingen: Göttingen, Sweden, 1980.

(9) Sinn, E.; O'Connor, C. J. *Inorg. Chim. Acta* 1979, 32, 29.

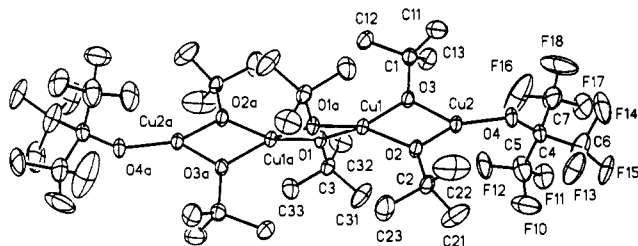
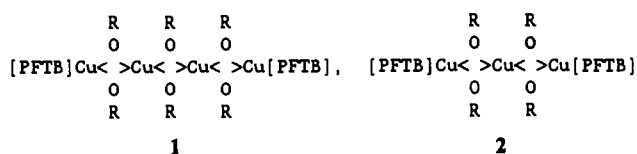
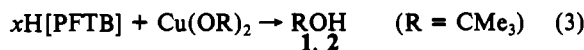


Figure 1. Thermal ellipsoid plot of **1** drawn from experimental coordinates.

or cellulose acetate capsules which were sealed in wax in a Vacuum Atmospheres Dri-Lab before being transferred to the cryostat and subjected to a series of evacuations and helium purges. The raw data were corrected for the susceptibility of the holder, converted to molar susceptibilities, and corrected for the diamagnetism of the component atoms by Pascal's constants.<sup>10</sup> The magnetic moments were calculated with the equation  $\mu = 2.828 (\chi_M T)^{0.5}$ . The molar susceptibilities were fitted to the appropriate theoretical equation, using a value of  $60 \times 10^{-6}$ /Cu for the TIP term, to determine the values of  $g$  and  $J$  (the coupling constant) by means of a nonlinear regression analysis program, Grafit (SIGMA Chemical).  $\chi^2$  values for the regression fits for **1** and **2** were  $3.1 \times 10^{-9}$  and  $2.6 \times 10^{-9}$ , respectively.

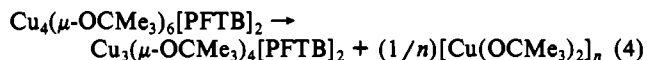
## Results and Discussion

**Synthesis and Characterization.** A single treatment of  $[\text{Cu}(\text{OCMe}_3)_2]_n$  with a moderate excess of  $\text{H}[\text{PFTB}]$  in hydrocarbon solvents resulted in the formation of **1** and **2** (eq 3). The relative



amounts of **1** and **2** produced were dependent on the reaction stoichiometry, where a 1:0.8 mole ratio produced mostly **1** and a 1:2.4  $[\text{Cu}(\text{OCMe}_3)_2]_n \cdot \text{H}[\text{PFTB}]$  mole ratio produced mostly **2**. Very little additional *tert*-butoxy replacement occurred with a single-alcohol treatment, but when the *tert*-butyl alcohol product was first removed, a second aliquot of  $\text{H}[\text{PFTB}]$  reacted with the mixture of **1** and **2** to form a mixture of products in addition to **1** and **2** which were not identified. The use of insufficient  $\text{H}[\text{PFTB}]$  to convert all the  $[\text{Cu}(\text{OCMe}_3)_2]_n$  to **1** resulted in the presence of unreacted  $[\text{Cu}(\text{OCMe}_3)_2]_n$  rather than longer chain  $\text{Cu}_m(\mu\text{-OCMe}_3)_{2m-2}[\text{PFTB}]_2$  species. A reaction between the less bulky  $\text{H}[\text{HFTB}]$  and  $[\text{Cu}(\text{OCMe}_3)_2]_n$  could be driven as far as 50% replacement, affording  $[\text{Cu}(\text{OCMe}_3)[\text{HFTB}]]_n$  (**3**).

Compound **1** was identified by its crystal structure (Figure 1). Although crystals of the more soluble **2** were not obtained, its solution NMR spectra were clearly consistent with the above representation, with the PFTB groups placed at the end of a linear chain. The NMR spectra of **3** were too complex for definite conclusions to be made. As one would expect, **2** had one  $^{19}\text{F}$  and one  $^1\text{H}$  peak, while **1** had one  $^{19}\text{F}$  peak and two  $^1\text{H}$  resonances in a 2:1 ratio. Although **2** is sublimable under vacuum, attempts to sublime **1** resulted in conversion to **2** and a  $[\text{Cu}(\text{OCMe}_3)_2]_n$  residue (eq 4). Conversion of **1** to **2** also occurred in solution.



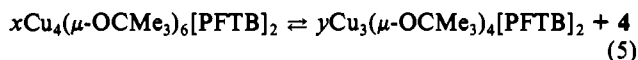
Solution NMR spectra of **1** (for example, Figure 2) showed substantial amounts of **2** even though elemental analysis, X-ray crystallography, and magnetic measurements (discussed later) showed no evidence for **2** in crystalline **1** prior to dissolution. Two equally intense peaks in the  $^1\text{H}$  spectrum corresponding to an

Table I. Crystal and Refinement Data

formula	$\text{C}_{32}\text{H}_{54}\text{Cu}_4\text{O}_8\text{F}_{18}$	space group	$\text{P}\bar{1}$ (No. 2)
fw	1162.9	temp, °C	22
$a$ , Å	10.609 (3)	$\lambda$ , Å	0.71073 (Mo K $\alpha$ )
$b$ , Å	10.667 (3)	$d_{\text{calcd}}$ , g cm $^{-3}$	1.593
$c$ , Å	11.151 (3)	$\mu$ , cm $^{-1}$	18.43
$\alpha$ , deg	100.69 (3)	$F(000)$	588
$\beta$ , deg	95.37 (3)	$R(F)^a$	0.068
$\gamma$ , deg	99.65 (3)	$R_w(F)^b$	0.056
$V$ , Å $^3$	1212.3 (7)	$Z$	1

$$^a R = \sum |F_o - F_c| / \sum |F_o|. \quad ^b R_w = [\sum w(F_o - F_c)^2 / \sum w(F_o)^2]^{1/2}.$$

unidentified species (**4**) were also present. There was some concentration dependence, as the relative amount of **2** increased as the overall concentration was decreased. Part of this increase at low concentrations can be explained by trace amounts of water in the solvent, which preferentially attack the  $\text{OCMe}_3$  groups, forming  $\text{HOCMe}_3$ , **2**, and a precipitate. A controlled-hydrolysis experiment confirmed that hydrolysis can convert **1** to **2**. However, hydrolysis cannot explain the presence of substantial amounts of **2** in solution at higher concentrations. Nor can it explain variation in the relative amounts of **1**, **2**, and **4** with temperature. An equilibrium process apparently takes place (eq 5). Two obvious



possible identities for **4** are a longer chain species such as  $\text{Cu}_5(\mu\text{-OCMe}_3)_8[\text{PFTB}]_2$  and a soluble form of  $[\text{Cu}(\text{OCMe}_3)_2]_n$ . While the former is consistent with the  $^1\text{H}$  spectra, the lack of any extra  $^{19}\text{F}$  peaks weighs against this possibility. The latter is unknown, and one would expect it to quickly oligomerize and precipitate as insoluble  $[\text{Cu}(\text{OCMe}_3)_2]_n$ . We were not able to identify **4** with the data available.

The NMR spectra of **1** and **2** have some interesting features. Large isotropic shifts were evident in both the  $^1\text{H}$  and  $^{19}\text{F}$  spectra, but NMR lines for **1** and **2** were surprisingly sharp ( $\nu_{1/2} = 45\text{--}90$  Hz) in comparison to those for other copper(II) *tert*-butoxides such as  $[\text{NaCu}(\text{OCMe}_3)_3]_{2,3}$  and  $\text{Ba}[\text{Cu}(\text{OCMe}_3)_3]_2$  and fluorinated *tert*-butoxides such as  $\text{Ba}[\text{Cu}[\text{HFTB}]_3]_2$  and  $[\text{Cu}_4\text{-}[\text{PFTB}]_7]_2$ ,<sup>4</sup> whose proton line widths ranged from 370 to 1200 Hz and whose  $^{19}\text{F}$  line widths ranged from 1800 to 2500 Hz. The  $^1\text{H}$  but not the  $^{19}\text{F}$  spectra of **3** show similar narrow lines. Both these sharp NMR lines and the lack of an ESR spectrum down to  $-196$  °C were indicative of a short electron relaxation time, which has been observed in multinuclear and compressed tetrahedral Cu(II) systems.<sup>11</sup>

**Crystal Structure of 1.** Crystal data and atomic coordinates for **1** are listed in Tables I and II, respectively, and selected bond distances and bond angles are listed in Table III. The tetranuclear Cu(II) complex consists of three  $\text{Cu}_2\text{O}_2$  linked twisted rings with bridging  $\text{OCMe}_3$  groups and two terminal PFTB groups. The complex has an inversion center, and only half of the molecule is crystallographically unique. The interior  $\{\text{Cu}_4\}$  chromophores are regular compressed tetrahedra whereas the exterior  $\{\text{CuO}_3\}$  chromophores are 3-coordinated, Y-shaped, and planar (maximum deviation from a least-squares plane through  $\text{O}(4)\text{--Cu}(2)\text{--O}(2)\text{--O}(3)$  is 0.047 Å and mean deviation is 0.023 Å). This unusual Cu(II) geometry has been previously observed<sup>4</sup> only for  $\text{Ba}[\text{Cu}[\text{HFTB}]_3]_2$ , a complex with similar steric restrictions. The exactly planar central  $\text{Cu}_2\text{O}_2$  ring forms a dihedral angle of 49.8° with each of the two terminal  $\text{Cu}_2\text{O}_2$  rings (maximum deviations form a least-squares plane 0.043 and 0.041 Å), and the coppers are distributed approximately linearly. The  $\text{Cu}(2)\text{--Cu}(1)\text{--Cu}(1a)$  angle is 171.3°. There is evidence for multiple bonding within the  $\{\text{CuO}_3\}$  chromophore. In polynuclear oxygen-bridged Cu(II)

(11) (a) Fritz, H. P.; Golla, B. M.; Keller, H. J.; Schwarzshans, K. E. *Z. Naturforsch.* 1966, 21B, 725-728. (b) Gojon, E.; Gaillard, J.; Latour, J.; Laugier, J. *Inorg. Chem.* 1987, 26, 2046-2052. (c) Swift, T. J. In *NMR of Paramagnetic Molecules*; LaMar, G. N., Horrocks, W. DeW., Holm, R. H., Eds.; Academic Press: New York, 1973; Chapter 2.

(10) Earnshaw, A. *Introduction to Magnetochemistry*; Academic Press: New York, 1968.

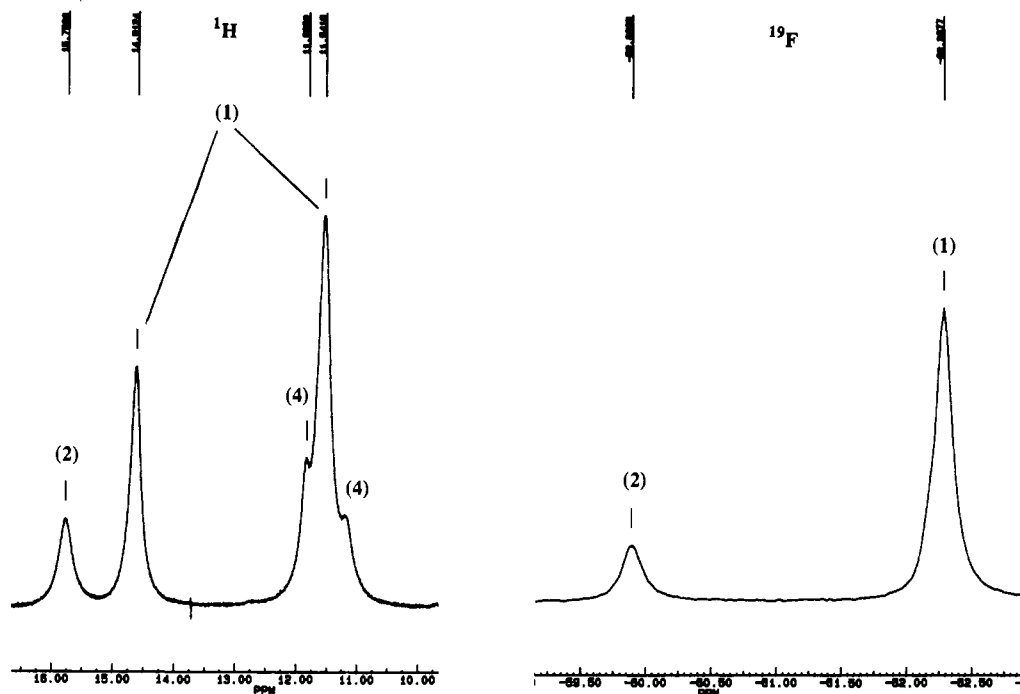


Figure 2. Proton and fluorine NMR spectra of **1** at room temperature.

Table II. Atomic Coordinates ( $\times 10^4$ ) and Equivalent Isotropic Displacement Coefficients ( $\text{\AA}^2 \times 10^3$ )

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq) <sup>a</sup>
Cu(1)	-444 (1)	901 (1)	-707 (1)	46 (1)
Cu(2)	-1465 (1)	2354 (1)	-2416 (1)	56 (1)
O(1)	-954 (3)	-876 (3)	-505 (3)	50 (1)
O(2)	124 (4)	2014 (4)	-1866 (3)	60 (2)
O(3)	-2034 (4)	1445 (4)	-1230 (3)	57 (2)
O(4)	-2278 (4)	3223 (4)	-3382 (4)	67 (2)
C(1)	-2979 (6)	1867 (7)	-481 (6)	68 (3)
C(11)	-2754 (9)	3315 (8)	-193 (8)	117 (5)
C(12)	-2847 (7)	1329 (8)	693 (6)	91 (4)
C(13)	-4307 (6)	1295 (9)	-1209 (7)	105 (4)
C(2)	1213 (6)	2217 (7)	-2523 (6)	62 (3)
C(21)	810 (8)	1774 (12)	-3856 (7)	157 (6)
C(22)	1744 (10)	3587 (9)	-2264 (11)	202 (8)
C(23)	2159 (8)	1449 (10)	-2139 (8)	141 (6)
C(3)	-1547 (6)	-1934 (6)	-1522 (5)	59 (2)
C(31)	-1196 (10)	-1601 (7)	-2699 (6)	130 (5)
C(32)	-2996 (7)	-2100 (8)	-1532 (8)	111 (4)
C(33)	-1109 (7)	-3158 (6)	-1338 (7)	94 (4)
C(4)	-3006 (6)	2977 (6)	-4490 (6)	62 (3)
C(5)	-3094 (11)	1602 (9)	-5212 (10)	125 (6)
F(10')	-2267 (32)	979 (42)	-4791 (41)	150
F(11')	-4071 (35)	1199 (43)	-4450 (33)	150
F(12')	-3755 (57)	1153 (76)	-6319 (29)	150
F(10)	-1890 (9)	1635 (10)	-5738 (8)	173 (6)
F(11)	-4032 (9)	1243 (11)	-6122 (6)	122 (4)
F(12)	-3137 (10)	748 (5)	-4544 (7)	133 (4)
C(6)	-2420 (11)	3946 (12)	-5236 (8)	132 (6)
F(13')	-1644 (39)	4951 (33)	-4648 (35)	150
F(14')	-1529 (39)	3160 (39)	-5674 (34)	150
F(15')	-3202 (48)	3969 (64)	-6223 (41)	150
F(13)	-1206 (7)	4116 (12)	-5178 (8)	149 (5)
F(14)	-2782 (11)	5140 (6)	-4687 (7)	161 (5)
F(15)	-2923 (9)	3636 (11)	-6423 (6)	135 (5)
C(7)	-4395 (10)	3211 (12)	-4282 (9)	130 (6)
F(16')	-4454 (46)	4210 (36)	-3416 (33)	150
F(17')	-4634 (49)	3509 (48)	-5420 (32)	150
F(18')	-5122 (48)	2038 (27)	-4209 (45)	150
F(16)	-4939 (10)	2126 (18)	-3874 (12)	287 (10)
F(17)	-5161 (6)	3225 (9)	-5271 (7)	135 (4)
F(18)	-4304 (10)	4226 (13)	-3512 (10)	242 (7)

<sup>a</sup> Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized  $U_{ij}$  tensor.

complexes, Cu–O distances are typically in the range 1.91–1.97 Å;<sup>12</sup> however, in mononuclear Cu(II) complexes, Cu–O distances

Table III. Selected Bond Lengths (Å) and Bond Angles (deg)

Cu(1)–O(1)	1.943 (4)	Cu(1)–O(2)	1.978 (4)
Cu(1)–O(3)	1.948 (4)	Cu(1)–O(1a)	1.918 (4)
Cu(2)–O(2)	1.856 (4)	Cu(2)–O(3)	1.865 (4)
Cu(2)–O(4)	1.797 (5)	O(1)–C(3)	1.452 (6)
O(2)–C(2)	1.434 (8)	O(3)–C(1)	1.440 (8)
O(4)–C(4)	1.351 (7)		
O(1)–Cu(1)–O(2)	145.0 (2)	O(1)–Cu(1)–O(3)	105.7 (2)
O(2)–Cu(1)–O(3)	78.0 (2)	O(1)–Cu(1)–O(1a)	81.7 (1)
O(2)–Cu(1)–O(1a)	111.3 (2)	O(3)–Cu(1)–O(1a)	152.5 (2)
O(2)–Cu(2)–O(3)	83.3 (2)	O(2)–Cu(2)–O(4)	144.8 (2)
O(3)–Cu(2)–O(4)	131.5 (2)	Cu(1)–O(1)–C(3)	122.7 (3)
Cu(1)–O(1)–Cu(1a)	98.3 (1)	C(3)–O(1)–Cu(1a)	126.1 (4)
Cu(1)–O(2)–Cu(2)	98.8 (2)	Cu(1)–O(2)–C(2)	136.1 (4)
Cu(2)–O(2)–C(2)	121.9 (4)	Cu(1)–O(3)–Cu(2)	99.5 (2)
Cu(1)–O(3)–C(1)	127.9 (4)	Cu(2)–O(3)–C(1)	120.7 (4)
Cu(2)–O(4)–C(4)	138.5 (4)		

have been observed in the 1.83–1.89-Å range.<sup>2c,d</sup> Here the reduction in coordination at Cu(2) results in a shortening of the Cu(2)–O(4) = 1.797 (5) Å bond to the unshared PFTB ligand as well as a shortening of the bonds to the shared OCMe<sub>3</sub> ligands [Cu(2)–O(3) = 1.865 (4) Å, Cu(2)–O(2) = 1.856 (4) Å]. In addition, the C(4)–O(4) bond distance in the PFTB ligand is 1.351 (7) Å, which is typical of C–O bonds with partial double-bond character.<sup>13</sup> In the previously cited Ba–Cu(II) complex,<sup>4</sup> Cu–O = 1.781 (7) Å to the unshared ligand and 1.878 (7) and 1.889 (6) Å to the shared ligands and C–O = 1.35 (2) Å. A comparable bonding geometry has been observed for Zn complexes with bulky ligands;<sup>14</sup> [RZnO(2,6-*i*-Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>2</sub>], [RZnO(2,4,6-*t*-Bu<sub>3</sub>C<sub>6</sub>H<sub>2</sub>)<sub>2</sub>], and [Zn<sub>3</sub>O(2,6-*i*-Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>4</sub>R<sub>2</sub>] (where R = CH<sub>2</sub>SiMe<sub>3</sub>) and [(Me<sub>2</sub>PhSi)<sub>3</sub>CZnOH]<sub>2</sub><sup>15</sup> have 3-coordinate planar geometries with

- (12) (a) Ahlgr n, M.; Turpeinen, U.; H m l inen, R. *Acta Crystallogr.* **1982**, *B38*, 429–433. (b) Bencini, A.; Gatteschi, D.; Zanchini, C. *Inorg. Chem.* **1985**, *24*, 700–703. (c) Charlot, M. F.; Jeanin, S.; Jeanin, Y.; Kahn, O.; Lucrece-Abaul, J.; Martin-Frere, J. *Inorg. Chem.* **1979**, *18*, 1675–1681. (d) Karlin, K. D.; Gultneh, Y.; Hayes, J. C.; Zubieta, J. *Inorg. Chem.* **1984**, *23*, 519–521. (e) Lewis, D. L.; Hatfield, W. E.; Hodgson, D. J. *Inorg. Chem.* **1974**, *13*, 147–152. (f) Majeste, R. J.; Meyers, E. A. *J. Phys. Chem.* **1970**, *74*, 3497–3500. (g) Schlemper, E. O.; Patterson, C.; Stunkel, J. *Acta Crystallogr.* **1989**, *C45*, 199–201.
- (13) Sutton, S. E. *Interatomic Distances Supplement*; Special Publication No. 18; The Chemical Society: London, 1965.
- (14) Olmstead, M. M.; Power, P. P.; Shoner, S. C. *J. Am. Chem. Soc.* **1991**, *113*, 3379–3385.

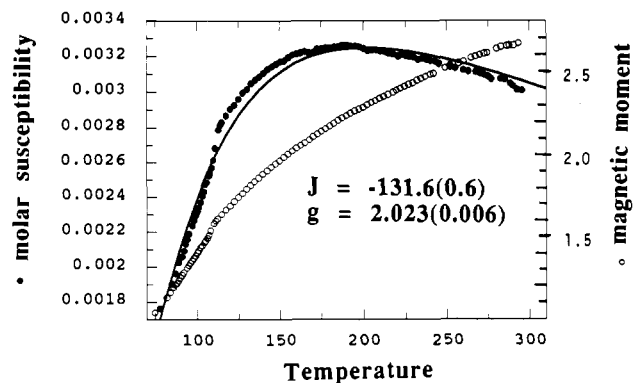


Figure 3. Magnetic susceptibility data for  $\text{Cu}_4(\mu\text{-OCMe}_3)_6[\text{PFTB}]_2$  (1).

similar bond shortening. The remaining bond distances are normal, with average C–C = 1.51 (3) Å and average C–F = 1.34 (7) Å. The large spread in the C–F distances is due primarily to the disorder in the  $\text{CF}_3$  groups. The Cu–Cu separations within the complex are Cu(1)–Cu(2) = 2.911 (1) Å and Cu(1)–Cu(1a) = 2.920 (1) Å, which are in the range (2.85–3.27 Å) observed<sup>12</sup> in oxygen-bridged polynuclear Cu(II) complexes. There are no intermolecular contacts shorter than normal van der Waals separations.

**Magnetic Measurements.** A plot of the molar susceptibility and moment vs temperature for **1** is shown in Figure 3. The prominent feature of this plot is the broad susceptibility maximum between 180 and 200 K, which is indicative of an antiferromagnetic interaction. The experimental susceptibility could not be fitted to the Bleaney–Bowers equation, in which the molecule is treated as a pair of noninteracting antiferromagnetic dinuclear subunits, nor could it be satisfactorily fitted to a modified form of the Bleaney–Bowers equation which allows for a slight interaction between dinuclear subunits.<sup>16</sup> This fact and the structure of the complex suggest that all 1–2 pairwise interactions are significant and need to be considered. Symmetry considerations dictate that there are two exchange interactions:  $J_1$ , which describes the Cu(1)–Cu(2) and Cu(1a)–Cu(2a) interactions, and  $J_2$ , for the Cu(1)–Cu(1a) interaction. Longer range 1–3 coupling and 1–4 interactions are possible but were not included in the analysis, as they were thought to be much smaller than the 1–2 interactions and it was desired to avoid overparametrization of the problem. The susceptibility data were fitted to the theoretical equation of Willett<sup>17</sup> for a linear, centrosymmetric copper tetramer with  $J_1 = J_2$ , to give the “ $g$ ” and  $J$  values shown on the figure. No correction was made for the possible contamination of this sample by the trinuclear complex (see synthesis discussion), since the low-temperature data do not show any susceptibility increase with decreasing temperature, which is the observed behavior of this species (see below). The latter provides further support for the presence of **2** in solution being due to an equilibrium rather than sample contamination.

The values of the coupling constants in other copper(II) hydroxide, alkoxide, and phenoxide dinuclear complexes have been shown to depend on structural type and the Cu–O–Cu bridging angle.<sup>18</sup> The strongest coupling is observed when the 4- or 5-coordinate copper atoms have their orbitals coplanar and overlap with the bridging oxygen atom. It is necessary to consider the orientations of the magnetic orbitals (the orbitals containing

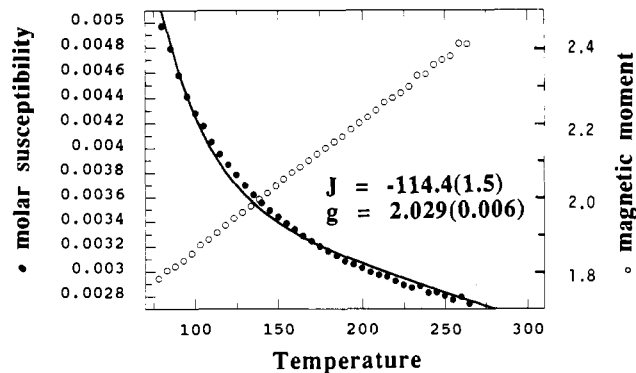


Figure 4. Magnetic susceptibility data for  $\text{Cu}_3(\mu\text{-OCMe}_3)_4[\text{PFTB}]_2$  (2).

unpaired electron density) in order to explain the magnetic results for this system. The 3-coordinate copper, Cu(2), has its  $d_{x^2-y^2}$  orbital as the active magnetic orbital, under the assumption that the  $x$  axis is  $45^\circ$  to the Cu(2)–Cu(1)–Cu(1a)–Cu(2a) axis and the Cu(2)–O(2)–O(3)–O(4) plane is the  $xy$  plane. This magnetic orbital should overlap well with O(2) and O(3) and thus foster strong coupling with Cu(1) if its magnetic orbital also overlaps well with O(2) and O(3). However, Cu(1) is in a distorted environment and its magnetic orbital (also  $d_{x^2-y^2}$  using same axes) will not overlap entirely with O(2) and O(3), which will reduce the coupling somewhat. The coupling between Cu(1) and Cu(1a) will be governed by the overlap of the magnetic orbitals of these atoms with O(1) and O(1a). Allowing  $J_1$  and  $J_2$  to take on different values did not improve the fit, but the Cu(1)–Cu(1a) interaction,  $J_2$  ( $-136.9$  (0.9)  $\text{cm}^{-1}$ ), is slightly greater than the Cu(1)–Cu(2) interaction,  $J_1$  ( $-133.7$  (0.3)  $\text{cm}^{-1}$ ), which suggests that the interior exchange pathway has slightly greater overlap.

The above argument pertains to the strength of the coupling but ignores the sign. Both ferromagnetic and antiferromagnetic doubly bridged copper dimers are known. Ferromagnetic compounds are observed over a small range of bridging angles with antiferromagnetic interactions existing to either side of this range and the magnitude of the coupling being a function of the actual value.<sup>19</sup> In a series of structurally related 4-coordinate alkoxide-bridged copper dinuclear complexes of the formula  $[\text{Cu}(\text{NH}_2\text{RO})\text{X}]_2$ , it was shown that the strength of the magnetic interaction increased with increasing Cu–O–Cu bridge angle, with  $J$  varying from  $-50$   $\text{cm}^{-1}$  at  $96.6^\circ$  to  $-400$   $\text{cm}^{-1}$  at  $104.5^\circ$ .<sup>20</sup> The average bridging angle of  $98.8^\circ$  in the present example is clearly in the antiferromagnetic regime, as observed.

A plot of the susceptibility and moment of the trinuclear complex (**2**) vs temperature is shown in Figure 4. The characteristic feature of an antiferromagnetically coupled copper trinuclear complex is a moment corresponding to one unpaired spin at low temperature which steadily rises with temperature to a limiting value of  $3g/2$ , as shown here. Analysis of the data by the theoretical equation<sup>21</sup> for three nonequivalent interacting copper(II) ions in which only adjacent interactions are considered yields the values of  $g$  and  $J$  shown on the figure. No provision was made in the analysis for the possible contamination of this sample by **1**, as there was no compelling reason to do so. The modest difference in the values of  $J$  for this compound and the tetranuclear complex could easily be explained by a small distortion, most likely a compression, in the Cu–O–Cu bridge angle or an increase in the dihedral angle between the best planes for adjacent copper atoms in the trinuclear complex from the anal-

(15) Al-Juaid, S. S.; Buttrus, N. H.; Eaborn, C.; Hitchcock, P. B.; Robert, A. T. L.; Smith, J. D.; Sullivan, A. C. *J. Chem. Soc., Chem. Commun.* **1986**, 908.  
 (16) (a) Bertrand, J. A.; Ginsberg, A. P.; Kaplan, R. I.; Kirkwood, C. E.; Martin, R. L.; Sherwood, R. C. *Inorg. Chem.* **1971**, *10*, 240. (b) Ginsberg, A. P.; Lines, M. E. *Inorg. Chem.* **1972**, *11*, 2289.  
 (17) Rubenacker, G. V.; Drumheller, J. E.; Emerson, K.; Willett, R. D. *J. Magn. Magn. Mater.* **1986**, *54*, 1483.  
 (18) (a) LeMay, H. E.; Hodgson, D. J.; Hodgson, J.; Pruetiangkura, P.; Theriot, L. J. *J. Chem. Soc., Dalton Trans.* **1979**, 781. (b) Calderazzo, F.; Marchetti, F.; Dell'Amico, G.; Pelizzi, G.; Colligiani, A. *J. Chem. Soc., Dalton Trans.* **1980**, 1419.

(19) Hay, P. J.; Thibault, J. C.; Hoffmann, R. *J. Am. Chem. Soc.* **1975**, *97*, 4884.  
 (20) (a) Pajunen, A.; Lehtonen, M. *Suom. Kemistil.* **1971**, *B44*, 200. (b) Lehtonen, M.; Uikkonen, E.; Uggla, R. *Suom. Kemistil.* **1971**, *B44*, 399. (c) Uggla, R.; Melnik, M.; Orama, O.; Klinga, M.; Harjulin, C. *Suom. Kemistil.* **1972**, *B45*, 323. (d) Pajunen, A.; Smolander, K. *Finn. Chem. Lett.* **1974**, 99. (e) Estes, E. D.; Hodgson, D. J. *Inorg. Chem.* **1975**, *14*, 334. (f) Nasakkala, M. *Ann. Acad. Sci. Fenn., Ser. A2* **1977**, 181.  
 (21) (a) Gruber, S. J.; Harris, C. M.; Sinn, E. *J. Chem. Phys.* **1968**, *49*, 2183. (b) Figgis, B. N.; Martin, D. J. *J. Chem. Soc., Dalton Trans.* **1972**, 2174.

ogous values of the tetranuclear complex; however, this is uncertain, since the structure of the former is unknown.

**Acknowledgment.** We thank Alan Berry (NRL) for helpful discussions and the ONR for financial support.

**Supplementary Material Available:** Complete tables of atomic coordinates, bond lengths, bond angles, hydrogen atom coordinates, anisotropic temperature factors, and temperature variation of chemical shifts (5 pages); a listing of structure factors (20 pages). Ordering information is given on any current masthead page.

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## Molecular Mechanics Calculations of Transition Metal Complexes

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Received July 24, 1991

A molecular mechanics force field appropriate for the modeling of Cu(II), Ni(II) ( $S = 1$ ), Co(III), Fe(III), Cr(III), Zn(II), and Rh(III) complexes with amine, carboxylate, pyridine, and thia ether ligands is presented in its entirety. The parameters comprising the force field were determined by matching a large number of strain-minimized structures with their corresponding crystal structures. Within the force field, the only parameters that were altered from one system to another were the strain-free bond length and the force constant of the metal-ligand bond. The calculations indicate that some corrections for electronic effects have to be applied in order to obtain a consistent force field.

### Introduction

Molecular mechanics calculations are a routine tool in organic chemistry<sup>1,2</sup> and are now well established in the area of coordination chemistry,<sup>3,4</sup> where they have most commonly been used for the computation of structures (analysis of disordered structures<sup>5</sup> and prediction of unknown structures<sup>6</sup>), isomer and conformer ratios,<sup>7</sup> and metal ion selectivities.<sup>8</sup> A majority of studies have dealt with cobalt(III) hexaamines where a well-established force field is available,<sup>9</sup> and until recently, we too have been concerned solely with such systems. However, our present interest in the design of chiral systems applicable to racemate separations based on enantioselective ligand exchange,<sup>10,11</sup> the determination of solution structures of dimeric Cu(II) complexes,<sup>12</sup> and the interpretation and prediction of chromophores of transition metal ions demanded the establishment of a force field for systems other than cobalt(III) hexaamine complexes.

It has been a popular belief that metal-ligand (M-L) force constants may be obtained directly from vibrational spectra. However, one has to realize that experimental force constants are molecule-specific quantities and therefore dependent on the environment of the respective molecules, whereas molecular mechanics calculations require more general parameters. Moreover, the spectroscopic force constants apply to situations involving

relatively small amplitude vibrations about a particular M-L value that may deviate considerably from the strain-free bond length. On the other hand, molecular mechanics calculations are concerned with large perturbations on a strain-free geometry. This leads to the view that molecular mechanics force constants do not necessarily represent experimentally available physical constants. Indeed, there are cases where molecular mechanics calculations have been performed based on concepts which have completely neglected the usually applied set of parameters based on the connectivity of the molecule.<sup>13</sup>

Force fields for several transition metal complexes have been reported including Co(III),<sup>9</sup> Co(II),<sup>14</sup> Ni(II) (both  $S = 1^{15}$  and  $S = 0^{16}$ ), Cu(II),<sup>17</sup> and Pt(II),<sup>18</sup> although the variety of ligands considered in some of these studies tended to be rather limited. In this paper, we present force field parameters for transition metal complexes of Cr(III), Fe(III) ( $S = 1/2$ ), Co(III), Ni(II) ( $S = 1$ ), Cu(II), Zn(II), and Rh(III) with various combinations of amine, pyridine, carboxylate, and thia ether ligands. It has not been our aim to develop an "ultimate" force field that would describe all metal-ligand interactions for all types of donor atoms, but instead we have concentrated on ligands containing the more typical "hard" donor atoms N and O and have dealt with soft donors such as S to a lesser extent. Nevertheless, the force field presented here is, we believe, either a significant improvement on previously reported force fields or it represents the first attempt to model a particular class of coordination compound with molecular mechanics.

### Experimental Section

The calculations were performed with the strain minimization program MOMECS7.<sup>19</sup> Within the molecular mechanics framework, the structure

- (1) Allinger, N. L. *Adv. Phys. Org. Chem.* **1976**, *13*, 1.
- (2) Allinger, N. L. *J. Am. Chem. Soc.* **1977**, *99*, 8127.
- (3) Snow, M. R. *J. Am. Chem. Soc.* **1970**, *92*, 3610.
- (4) Hancock, R. D. *Prog. Inorg. Chem.* **1989**, *37*, 187.
- (5) Boeyens, J. C. A.; Fox, C. C.; Hancock, R. D. *Inorg. Chim. Acta* **1984**, *87*, 1.
- (6) Bernhardt, P. V.; Comba, P. *Helv. Chim. Acta* **1991**, *74*, 1834; **1992**, *75*, 645.
- (7) Yamaguchi, M.; Yamamatsu, S.; Furusawa, T.; Yano, S.; Saburi, M.; Yoshikawa, S. *Inorg. Chem.* **1980**, *19*, 2010.
- (8) Hancock, R. D.; Ngwenya, P. W.; Evers, A.; Wade, P. W.; Boeyens, J. C. A. *Inorg. Chem.* **1990**, *29*, 264.
- (9) Hambley, T. W.; Hawkins, C. J.; Palmer, J. A.; Snow, M. R. *Aust. J. Chem.* **1981**, *34*, 45.
- (10) Comba, P.; Hörmann, A.; Martin, L. L.; Zipper, L. *Helv. Chim. Acta* **1990**, *73*, 874.
- (11) Bernhardt, P. V.; Comba, P.; Gyr, T.; Várnagy, K. *Inorg. Chem.* **1992**, *31*, 1220.
- (12) Bernhardt, P. V.; Comba, P.; Hambley, T. W.; Massoud, S. S.; Stebler, S. *Inorg. Chem.*, following paper in this issue.

- (13) Saunders, M.; Jarret, R. M. *J. Comput. Chem.* **1986**, *7*, 578.
- (14) Bond, A. M.; Hambley, T. W.; Snow, M. R. *Inorg. Chem.* **1985**, *24*, 1920.
- (15) McDougall, G. J.; Hancock, R. D.; Boeyens, J. C. A. *J. Chem. Soc., Dalton Trans.* **1978**, 1438.
- (16) Hancock, R. D.; Dobson, S. M.; Evers, A.; Ngwenya, M. P.; Wade, P. W.; Boeyens, J. C. A.; Wainwright, K. P. *J. Am. Chem. Soc.* **1988**, *110*, 2788.
- (17) Hancock, R. D.; Dobson, S. M.; Boeyens, J. C. A. *Inorg. Chim. Acta* **1987**, *133*, 221.
- (18) Hambley, T. W. *Inorg. Chem.* **1988**, *27*, 1073.
- (19) Hambley, T. W. *MOMECS7, A Program for Strain Energy Minimization*; University of Sydney: Sydney, Australia, 1987.