Inorg. Chem. **1996,** *35,* 5966−5967

Helical Antiferromagnetic Copper(II) Chains with a Collagen Structural Motif

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Received June 14, 1996

A major part of supramolecular chemistry[1] deals with the helical structural motif because of its importance in biological systems and in asymmetric catalysis.[2,3] Among the helical biomolecules, collagen is one of the most abundant proteins in mammals and is distinctive in forming high tensile strength fibers. A collagen helical strand differs from the α-helix[4] in that (i) the structure is stabilized not by H-bonding, as in the α-helix, but by the steric demands of its pyrrolidone rings and (ii) the collagen helix is more open (higher-pitched) than the α-helix. The synthesis[5] and X-ray structural study[6] of the model homopolypeptide poly(L-proline) led the way to a spurt of investigations[7] involving this and related compounds. Here we report the synthesis,[8] X-ray crystal structure,[9] and magnetic properties of an infinite helical chain of a Cu(II)−thioether−carboxylate complex, $[CuL]_n(H_2O)_n$, **1**, an "inorganic" analogue of collagen's topology.

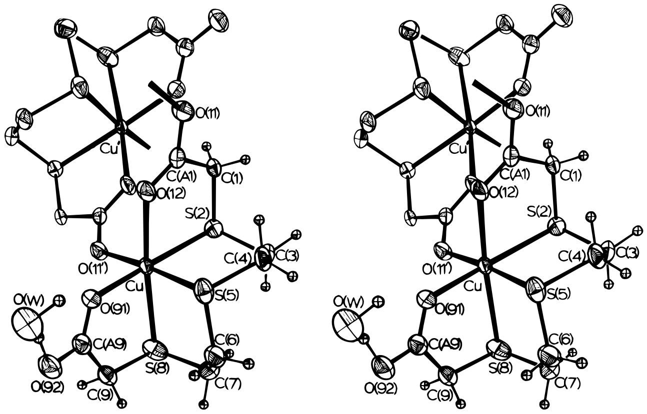
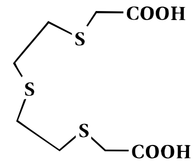


Figure 1. ORTEP stereoview of the Cu−ligand unit in $[CuL]_n(H_2O)_n$, **1**. Selected bond lengths (Å) and angles (deg): Cu−S(2) 2.459(1), Cu−S(5) 2.357(1), Cu−S(8) 2.596(1), Cu−O(91) 2.028(2), Cu−O(12) 2.220(2), Cu−O(11′) 1.969(2); S(2)−Cu−S(5) 88.52(2), S(2)−Cu−O(11′) 96.60(6), O(11′)−Cu−O(91) 89.51(8), O(91)−Cu−S(5) 85.40(6), O(12)−Cu−S(2) 80.57(5), O(12)−Cu−S(8) 170.87(6), O(12)−Cu−O(11′) 96.95(8).



H_2L

The structure (Figure 1) consists of infinite chains of roughly octahedrally coordinated copper(II)−ligand units linked by Cu−O bonds. Each doubly deprotonated ligand acts as pentadentate to one copper(II) and as monodentate to a neighboring copper(II) center. The three sulfur donor atoms are coordinated to the corners of one of the triangular faces of the pseudo-octahedron. Two oxygen atoms (O(11) and O(12)) of one of the two carboxylate groups bridge two copper(II) centers, while the second carboxylate group is monodentate with a noncoordinated oxygen atom hydrogen bonded to a water molecule. Bond distances between the bridging carboxylate oxygen and copper(II) atoms are 1.969(2) (Cu−O(11′)) and 2.220(2) (Cu−O(12)) Å. While the Cu−O(11) distance is comparable to the commonly observed[13] bond lengths between bridging carboxylate oxygen and copper(II), the Cu−O(12) distance is some-

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(1) General references: (a) Amabillino, D. B.; Stoddart, J. F. *Chem. Rev.* **1995**, *95*, 2725. (b) Lehn, J.-M. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1304. (c) Fabrizzi, L., Poggi, A., Eds. *Transition Metals in Supramolecular Chemistry*; Kluwer Academic: Dordrecht, 1994.

(2) Corey, E. J.; Cymin, C. L.; Noe, M. C. *Tetrahedron Lett.* **1994**, *35*, 69.

(3) Maruoka, K.; Murase, N.; Yamamoto, H. *J. Org. Chem.* **1993**, *58*, 2938.

(4) Stryer, L. *Biochemistry*, 3rd ed.; W. H. Freeman and Co.: New York, 1988.

(5) Fasman, G. D.; Blout, E. R. *Biopolymers* **1963**, *1*, 3.

(6) (a) Traub, W.; Shmueli, U. *Nature* **1963**, *198*, 1165. (b) Cowan, P. M.; McGavin, S. *Nature* **1964**, *176*, 501.

(7) For example: (a) Middendorf, H. D.; Hayward, R. L.; Parker, S. F.; Bradshaw, J.; Miller, A. *Biophys. J.* **1995**, *69*, 660. (b) Ogawa, M. Y.; Moriera, I.; Wishart, J. F.; Isied, S. S. *Chem. Phys.* **1993**, *176*, 589. (c) Caswell, D. S.; Spiro, T. G. *J. Am. Chem. Soc.* **1987**, *109*, 2796. (d) Shearer, G. M.; Mozes, E.; Sela, M. *J. Exp. Med.* **1971**, *133*, 216. (e) Tonelli, A. E. *J. Am. Chem. Soc.* **1970**, *92*, 6187. (f) Strassmair, H.; Engel, J.; Zundel, G. *Biopolymers* **1969**, *8*, 237.

(8) A 1 mmol quantity of $CuSO_4{\cdot}5H_2O$ in 15 mL hot water was added with stirring to 1 mmol of Na_2L[10] in 15 mL of hot water, giving a deep green solution. After the solution was allowed to cool and stand undisturbed for 2 days, apple-green diffraction-quality crystals were produced, which were filtered off, washed with water, and air-dried. Analyses for C and H were satisfactory.

(9) Crystal data for $[CuL]_n(H_2O)_n$, **1**: $C_8H_{14}O_5S_3Cu$, $M = 350$, monoclinic, space group $P2_1/c$, $a = 7.787(1)$ Å, $b = 6.266(1)$ Å, $c = 25.737(7)$ Å, $\beta = 97.92(1)°$, $V = 1244$ Å^3, $D_c = 1.87$ g cm^{-3}, $Z = 4$, μ(Mo Kα) = 23.1 cm^{-1}, λ(Mo Kα) = 0.710 69 Å. Single-crystal X-ray diffraction data were collected on an Enraf-Nonius four-circle CAD-4 diffractometer at room temperature. The $\omega-2\theta$ scan technique was used as previously described,[11] to record the intensities for all nonequivalent reflections for which $1° < 2\theta < 54°$. The raw intensity data were corrected for Lorentz−polarization effects and absorption. Of the 3095 independent intensities, there were 2655 with $F_o^2 > 3\sigma F_o^2$, where σF_o^2 was estimated from counting statistics.[12] A three-dimensional Patterson synthesis was used to determine the heavy-atom positions, which phased the data sufficiently well to permit location of the remaining non-hydrogen atoms from Fourier syntheses. Full-matrix least-squares refinement was carried out as previously described.[11] Anisotropic temperature factors were introduced for the non-hydrogen atoms. Further Fourier difference functions permitted location of the hydrogen atoms, which were included in the refinement for four cycles of least-squares refinement and then held fixed. The model converged with $R = 0.043$ and $R_w = 0.060$. A final Fourier difference map was featureless.

(10) Addison, A. W.; Rao, T. N.; Wahlgren, C. G. *J. Heterocycl. Chem.* **1983**, *20*, 1481.

(11) Freyberg, D. P.; Mockler, G. M.; Sinn, E. *J. Chem. Soc., Dalton Trans.* **1976**, 447.

(12) Corfield, P. W. R.; Doedens, R. J.; Ibers, J. A. *Inorg. Chem.* **1967**, *6*, 197.

(13) (a) Bürger, K.-S.; Chaudhuri, P.; Wieghardt, K. *J. Chem. Soc., Dalton Trans.* **1996**, 247. (b) Bürger, K.-S.; Chaudhuri, P.; Wieghardt, K.; Nuber, B. *Chem. Eur. J.* **1995**, *1*, 583. (c) Colacio, E.; Dominguez-Vera, J.-M.; Costes, J.-P.; Kivekäs, R.; Laurent, J.-P.; Ruiz, J.; Sundberg, M. *Inorg. Chem.* **1992**, *31*, 774.

S0020-1669(96)00709-4 CCC: $12.00

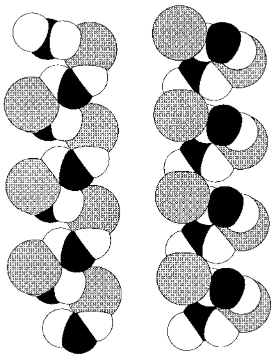

Figure 2. Space-filling diagram of two adjacent complementary helices in **1**. Only the −Cu−COO−Cu− backbone is shown, and hydrogen atoms are omitted for clarity.

what longer. The S(5)−Cu distance (2.357(1) Å), which is comparable to other reported[14] thioether−copper(II) distances, is the shortest among the three S−Cu bonds, and S(8)−Cu (2.596(1) Å) is the longest. The S(8)−Cu and O(12)−Cu bonds are thus elongated due to axial Jahn−Teller distortion.

Figure 2 shows the space-filling diagram of two antiparallel neighboring helical strands in **1** with −Cu−COO−Cu− backbones running along the *c* direction. In the lattice, right- and left- handed helices alternate, resulting in an optically inactive racemic crystal, spontaneous resolution of left- and right-handed helices in the solid state being rare.[15] For the helix in **1**, the number of repeating units per turn and the rise along the helix axis per repeating unit are 2 and 6.27 Å, respectively. The pitch, at 12.53 Å, is even greater than for poly(proline) (9.36 Å), which is the most open protein helix.[16] In **1**, the helix is exogenously decorated by the unidentate carboxylate and chelating ethylene−dithioether moieties in a fashion comparable with the disposition of pyrrolidone rings in the poly(proline) helix.

From the structure of **1**, a relationship between the bridging mode of carboxylate toward M^{n+} (M^{n+} is an octahedral metal ion) and helicity in the resulting structure is evident. For a carboxylate-bridged helical complex of M^{n+}, the bridges have to be oriented in a mutually *cis* fashion, *i.e.*, either in an equatorial−axial or in an equatorial−equatorial mode. Another copper(II) chain, with an equatorial−equatorial carboxylate bridging mode, has been indicated[13c] to have a "helix-like" structure. The present compound is also a constitutionally simpler (binary) compound, whereas the previously reported complex was, like most other helical metal-containing systems, a ternary system (including H_2O ligands[13c] essential to the structure).

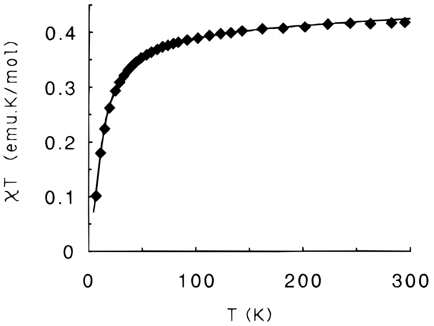

Figure 3. Variable-temperature magnetic data for **1**. The points ♦ represent the experimental data, and the solid line represents the theoretical fit calculated from $J = -5.4$ cm^{-1}, $g = 2.12$, $\rho = 0.00$, and TIP = 6.0×10^{-5} emu mol^{-1}.

Magnetic data between 7 and 294 K for a polycrystalline sample of **1** are displayed in Figure 3. The value of χT increases steadily with increase in temperature, from 0.1009 cm^3 mol^{-1} K at 7.1 K to 0.4185 cm^3 mol^{-1} K at 294.2 K, indicating antiferromagnetic behavior. The data can satisfactorily be fitted to the modified empirical function introduced by Hall to represent the Bonner−Fisher model for a uniformly spaced Heisenberg chain of spins with $S = {}^1/_2$.[17] The best fit gave $-J = 5.4$ cm^{-1}, $g = 2.12$, and $\rho = 0.0$. J values reported[13c,18] for two also weakly exchange-coupled carboxylato-bridged copper(II) chains are −1 and 3.3 cm^{-1}. Although it is difficult to correlate the sign of J with the structural parameters of carboxylate bonding in chain complexes from the available data, it is evident that equatorial−axial coupling of coppers(II) should lead to weak exchange, irrespective of the sign of the coupling constant.

Acknowledgment. A.W.A. and K.K.N. thank Drexel University for support.

Supporting Information Available: Tables of atomic coordinates, thermal parameters, bond distances, bond angles, and least-squares planes (5 pages). Ordering information is given on any current masthead page.

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(14) (a) Wilson, J. C.; Verweij, P. D.; Driessen, W. L.; Reedijk, J. *Inorg. Chim. Acta* **1992**, *192*, 219. (b) Benezekri, A.; Dubourdeaux, P.; Latour, J. M.; Laugier, J.; Rey, P. *Inorg. Chem.* **1988**, *27*, 1988. (c) Addison, A. W.; Burke, P. J.; Henrick, K.; Rao, T. N.; Sinn, E. *Inorg. Chem.* **1983**, *22*, 3645.

(15) Kawamoto, T.; Hammes, B. S.; Haggerty, B.; Yap, G. P. P.; Rheingold, A. L.; Borovik, A. S. *J. Am. Chem. Soc.* **1996**, *118*, 285.

(16) Dickerson, R. E.; Geis, I. *The Structure and Action of Proteins*; Harper & Row: Evanston, IL, 1969.

(17) (a) Bonner, J. C.; Fisher, M. E. *Phys. Rev.* **1964**, *A135*, 640. (b) Hall, J. W. Ph.D. Thesis, University of North Carolina (cited by: Hatfield, W. E. *J. Appl. Phys.* **1981**, *52*, 1985). (c) The empirical function has been modified to account for the presence of paramagnetic impurity (ρ) and temperature-independent paramagnetism, TIP (a constant value of 6.0×10^{-5} emu mol^{-1} assumed).

(18) Coughlin, P. K.; Lippard, S. J. *J. Am. Chem. Soc.* **1984**, *106*, 2328.