Inorg. Chem. **2003**, *42*, 2602–2605

Inorganic Chemistry

Article

Structural and Magnetic Behavior of the Kinked Chain $Cu(hfac)_2(tan)$ and Its Relevance to $Cu(NO_3)_2(tan)$ (hfac = Hexafluoroacetylacetonate; tan = 1,4,5-Triazanaphthalene)

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Received November 7, 2002

When stoichiometric amounts of $Cu(hfac)_2\cdot H_2O$ and 1,4,5-triazanaphthalene (tan) were combined in methanol, green crystals of $Cu(hfac)_2(tan)$ were formed. Its structure was determined at low temperature ($P2_1/c$; $a = 8.3308(4)$ Å, $b = 14.8945(7)$ Å, $c = 18.3046(10)$ Å, $\beta = 99.298(2)^\circ$, $V = 2241.5(3)$ Å^3) and found to consist of a novel kinked-chain arrangement where N atoms on opposite sides of the tan ligand bridge $Cu(hfac)_2$ moieties together. Long axial Cu–N bonds lead to rather weak ($J/k_B = -0.06(5)$ K) antiferromagnetic interactions according to a Bonner–Fisher fit of the magnetic susceptibility data. The magnetic behavior demonstrated by $Cu(hfac)_2(tan)$ contrasts markedly with that of $Cu(NO_3)_2(tan)$, as reported by Hatfield and co-workers, and is attributed to the differing orientations of the Cu $d_{x^2-y^2}$ magnetic orbital.

Introduction

Organic bridging ligands that contain nitrogen donor atoms have been used extensively to organize ions, particularly transition metals, into a variety of architectures. Among these types of ligands are pyrazine (pyz),[1] pyrimidine (pym),[2] and 4,4′-bipyridine (bipy).[3] More complex species that feature three or more potentially coordinating N atoms are also known; however, lower solubilities in common organic solvents have limited their application. Examples include, but are not limited to, 2,2′-bipyrimidine (bpym),[4] hexaazatriphenylene (hat),[5] and purine (pur).[6] It is noteworthy to point out that the aforementioned ligands typically form chelates with metal cations. In the case of nonchelating ligands, multiple bonding modes are often possible. This

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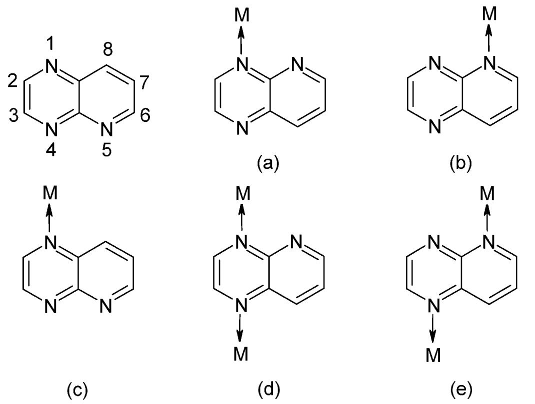
Chart 1



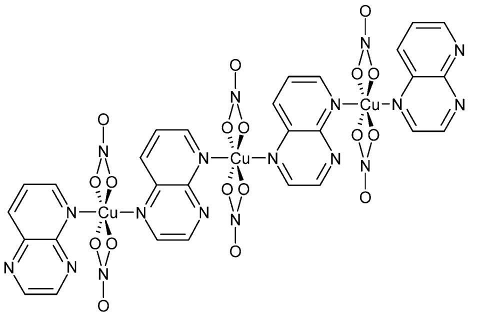
(a) (b) (c) (d) (e)

requires assessment of geometrical considerations, especially when the N atoms are in reasonably close proximity to one another.

An interesting molecule that has seldom been utilized in crystal engineering is 1,4,5-triazanaphthalene (herein denoted tan). As illustrated in Chart 1, tan has three different nitrogen atoms, each potentially capable of forming coordinate covalent bonds with transition-metal ions. Such possibilities render this ligand particularly amenable to the design and construction of multidimensional arrays. As anticipated, there are several possible coordination modes that tan may adopt: (a−c) it can coordinate in a monodentate fashion through any of the three nitrogen atoms, (d) it can coordinate to the two N atoms in the pyrazine ring, and (e) it can coordinate to the pyridine and pyrazine N atoms on opposite sides of the molecule. Fluxional behavior associated with the coordination ambiguity of 1,4,5-triazanaphthalene has been studied by high-resolution ^{1}H NMR spectroscopy, for example.[7]

Nearly 30 years ago, Hatfield and co-workers[8] employed tan as both a bridging ligand and superexchange mediator in Cu(NO$_3$)$_2$(tan). However, it was not possible to obtain single crystals suitable for X-ray diffraction. With evidence provided by electronic spectroscopy, magnetic susceptibility, and Hückel calculations, Hatfield postulated that the structure consisted of kinked chains where N(1) and N(5) coordinate to Cu^{2+} ions in an alternating fashion, as depicted in Chart 2. Strikingly, an exchange energy of −13.8 K was found, which is larger than that found in the linear chain Cu(NO$_3$)$_2$(pyz) (−10.6 K),[9] despite the longer superexchange path.

Chart 2



To gain further insight into the structure of Cu(NO$_3$)$_2$(tan), the related compound Cu(hfac)$_2$(tan) (hfac = hexafluoroacetylacetonate) has been synthesized and characterized by single-crystal X-ray diffraction and magnetic measurements. Cu(hfac)$_2$ was selected for this study because it is a good Lewis acid and has been demonstrated to readily coordinate to weak Lewis bases such as nitronyl nitroxides, e.g. Cu(hfac)$_2$(NpNN) (NpNN = *p*-nitrophenyl nitronyl nitroxide),[10] and sterically hindered aromatic amines, e.g. Cu(hfac)$_2$(qz) (qz = quinazoline).[2b]

Experimental Section

Synthesis. A 0.450 g (1.02 mmol) amount of Cu(hfac)$_2$·H$_2$O (Aldrich) was dissolved in 5 mL of methanol and slowly added to a 5 mL methanolic solution containing 0.134 g (1.02 mmol) of 1,4,5-triazanaphthalene (Acros) to give a dark green solution. A small amount of 2,2-dimethoxypropane was added to the reaction mixture to remove any residual water. Slow evaporation of the solution over a 2 week period afforded a large mass of dark green rods. They were collected via suction filtration and air-dried for 3 h to give 0.234 g of material in 38% yield. Anal. Calcd for $C_{17}H_7N_3O_4F_{12}Cu$: C, 33.54; H, 1.16; N, 6.90. Found: C, 33.28; H, 1.08; N, 6.67. Selected IR peaks (cm^{-1}): ν_{C-H} 2960 w, 2919 w; $\nu_{C=O}$:1641 s; $\nu_{C=C}$ 1598 m, 1557 m; $\nu_{C=N}$ 1481 s; ν_{C-F} 1256−1206 s; δ_{C-H} 790 s; γ_{Cu-N} 435 m, 410 m.

X-ray Crystallography. A green rod measuring 0.4 × 0.2 × 0.2 mm was glued to the end of a glass fiber and mounted on a Bruker AXS SMART diffractometer equipped with a CCD area detector. A hemisphere of diffraction data were collected at 150 K in order to minimize rotational disorder of the $-CF_3$ substituents of the hfac moieties. The detector frames were integrated by use of the program SAINT and the intensities corrected for absorption by Gaussian integration using the program SADABS. The structure solution was carried out using direct methods. Full-matrix least-squares refinement on F^2 (including all data) was performed using the program SHELXTL.[11] All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atom positions were located from difference Fourier maps but constrained to ideal geometries using a "riding" model. No correction for extinction was necessary.

Description of the Structure

Cu(hfac)$_2$(tan) crystallizes in the monoclinic space group $P2_1/c$ with $a = 8.3308(4)$ Å, $b = 14.8945(7)$ Å, $c = 18.3046$-

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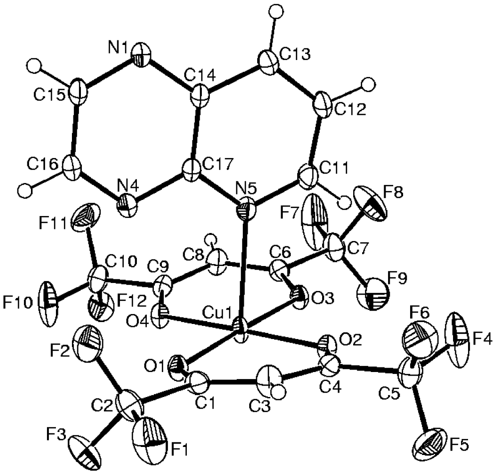

Figure 1. ORTEP drawing and atom-labeling scheme of the Cu coordination sphere for $Cu(hfac)_2(tan)$. Thermal ellipsoids are drawn at the 35% probability level.

(10) Å, $\beta = 99.298(2)°$, and $V = 2241.5(3)$ Å^3 at −123 °C. Four oxygen atoms from two hfac ligands chelate to the Cu^{2+} center, while the axial positions are occupied by N atoms of the tan ligand, as shown in Figure 1. The hfac ligands are tightly bound to the Cu^{2+} ion, resulting in four short Cu−O bond distances of 1.942(2), 1.961(2), 1.941(2), and 1.965(2) Å for Cu−O(1), Cu−O(2), Cu−O(3), and Cu−O(4), respectively. Because Cu^{2+} is Jahn−Teller active, it is expected to adopt a 4 + 2 coordination environment that features four short bond distances and two longer ones as commonly observed. The two axial Cu−N sites are indeed substantially longer at 2.528(2) Å (Cu−N(1)) and 2.466(2) Å (Cu−N(5)). The bond angles within the CuO_4N_2 chromophore deviate appreciably from 90° and range from 85.02(7) to 97.06(7)° for N(5)−Cu−O(2) and N(5)−Cu−O(4), respectively. Additionally, the N(5)−Cu−N(1) bond angle deviates slightly from perfect linearity at 172.77(7)°. All bond distances and angles within the hfac and tan ligands are typical of these species. The trifluoromethyl substituents are relatively static, in accord with the well-behaved thermal parameters. Previously, only one other structurally characterized compound containing tan was known, namely $Os_4H_4(CO)_{11}(tan)$, where the tan ligand is coordinated in a monodentate fashion through the pyridine nitrogen.[12]

Also of interest is the saddle shape adopted by the $Cu(hfac)_2$ species (Figure 1). A similar puckered structure has been observed in various metalloporphyrin donor−acceptor chains such as $[MnTPP][C_3(CN)_5]$.[13] It was suggested that geometric distortions such as this likely originate from steric effects imposed by the bulky asymmetrically bridging ligands. Recent work on iron porphyrins such as Fe(TMCP)Cl (TMCP = $\alpha,\beta,\alpha,\beta$-tetramethylchiroporphyrin),[14] Fe(QTPP)Cl (QTPP = quinoxalinotetraphenylporphyrin),[15] and Fe[T(*p*-Me)PP][PPh(OMe)$_2$]$_2$ (T(*p*-Me)PP = tetrakis(*p*-methylphenyl)porphyrin)[16] also reveal a similar distortion, albeit generally in the case of five-coordination and not six as in the title compound.

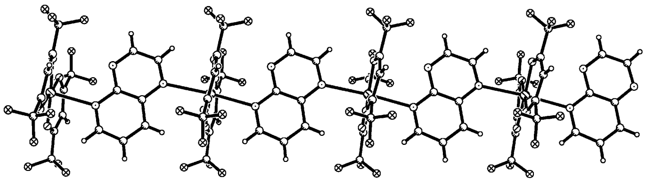

Figure 2. Kinked-chain arrangement as observed in $Cu(hfac)_2(tan)$. Note the slight saddle shape adopted by the $Cu(hfac)_2$ moiety.

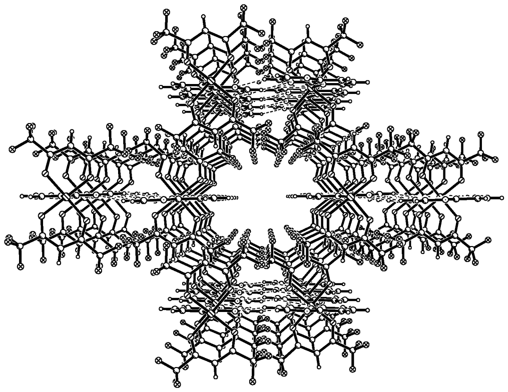

Figure 3. Chain packing diagram for $Cu(hfac)_2(tan)$ as viewed parallel to the *a* axis.

The extended structure of $Cu(hfac)_2(tan)$ consists of polymeric 1D chains that run parallel to the *a* axis (Figure 2), where the tan ligand links the $Cu(hfac)_2$ moieties together as shown in Chart 1e, with an intrachain Cu···Cu separation of 8.331 Å. The bonding configuration adopted by the tan ligand mandates a kinked-like motif. Importantly, this result is consistent with the mode favored by the extended Hückel calculations carried out for $Cu(NO_3)_2(tan)$.[8]

The 1D chains pack in a somewhat unusual fashion. Chains pack in “pairs” and run parallel to the *a* axis, as depicted in Figure 3. As a result of this crystal packing, voids are formed that are too small to accommodate solvent molecules. The chains are held together by energetically favorable molecular interactions among the perfluoroalkyl substituents, i.e., a fluorophilic effect, imparted by neighboring hfac ligands. These very weak intermolecular forces originate from the low polarizability of the fluorine atom.[17] The notion of fluorine segregation has been addressed in other compounds, such as the 1:2 donor−acceptor salt (BFPDT-TTF)[Ni(F_2pdt)$_2$]$_2$ (BFPDT-TTF = bis(2,2-difluoropropylenedithio)tetrathiafulvalene, F_2pdt = 6,6-difluoro-6,7-dihydro-5*H*-[1,4]dithiapine-2,3-dithiolate).[18]

Magnetic Behavior

The variable-temperature magnetic susceptibility of $Cu(hfac)_2(tan)$ was measured between 2 and 300 K using a

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Quantum Design MPMS-5S SQUID magnetometer. At room temperature $\chi_T(T)$ has a value of 0.44 emu K/mol and is slightly higher than the spin-only value of 0.38 emu K/mol expected for uncoupled $S = {}^1/_2$ ions. Such behavior is typical of Cu^{2+} ions that afford Landé g values in the range 2.05−2.25, depending on geometry and coordination environment.[19] $\chi_T(T)$ remains essentially invariant upon cooling further to 2 K. A fit of the data to the $S = {}^1/_2$ Bonner−Fisher uniform chain model yields $\langle g \rangle = 2.169(3)$ and $J/k_B = -0.06(5)$ K, indicating extremely weak antiferromagnetic interactions between the Cu^{2+} centers. This contrasts with the much stronger AFM coupling found in Cu(NO$_3$)$_2$(tan).[8] The weak interaction in Cu(hfac)$_2$(tan) likely originates from a combination of exceptionally long axial Cu−N bonds and minute overlap of the Cu $d_{x^2-y^2}$ magnetic orbital that is confined to the CuO$_4$ plane. A similar situation also occurs for Cu(NO$_3$)$_2$(pyz) and Cu(hfac)$_2$(pyz), and although they possess identical linear chain structures, they exhibit markedly different exchange couplings with J values of −10.6 and $\ll -1$ K, respectively.[9,20] Structural data for Cu(NO$_3$)$_2$(pyz) show that the Jahn−Teller axis lies along one of the O−Cu−O′ directions and not the chain axis, and while the structure of Cu(NO$_3$)$_2$(tan) is not known explicitly, the Cu^{2+} coordination sphere is likely similar.

Clearly the little used 1,4,5-triazanaphthalene ligand in coordination chemistry may lead to other novel structures in addition to the Cu(hfac)$_2$(tan) described here and should be explored further in light of the present findings. Use of an ambidentate organic base such as tan may generate a multitude of complex network structures of varying dimensionalities and, in turn, facilitate superexchange interactions between mutually coordinated paramagnetic building blocks.

Acknowledgment. Oak Ridge National Laboratory is managed by UT-Battelle, LLC, for the U.S. Department of Energy under Contract No. DE-AC05-00OR22725.

Supporting Information Available: X-ray crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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