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Corner Sharing Tetrahedral Network in $Co_3(HAT)[N(CN)_2]_6(OH_2)_2$ (HAT = 1,4,5,8,9,12-Hexaazatriphenylene)

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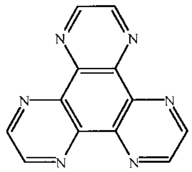
We report a trinuclear Co^{II} complex containing bridging dicyanamides and a tris-chelated HAT, which possesses ~37% void space. The magnetic exchange pathways appear in the structure as a corner sharing tetrahedral network. The compound crystallizes in the monoclinic space group $P2_1/c$ [$a = 13.655(3)$ Å, $b = 15.189(3)$ Å, $c = 22.367(4)$ Å, $\beta = 114.100(2)°$, $V = 4234.5(14)$ Å^3, $Z = 4$, $R(F_o) = 0.0823$]. The magnetic data were fit to an $S = {}^3/_2$ model for systems dominated by zero-field splitting effects with $g = 2.01$ and $D = 38.9$ cm^{-1}.

The HAT (1,4,5,8,9,12-hexaazatriphenylene) ligand and its derivatives were originally viewed as being useful for studies of photophysical properties,[1] liquid crystalline ordering,[2] chirality,[3] and DNA related chemistry.[4] More recently, HAT has been adopted by chemists studying supermolecular materials,[5] to create self-assembled, cagelike compounds, and by chemists studying magnetic materials, to probe for spin-frustrated or trimerlike behavior in systems containing metal ions.[6]



HAT

The Dunbar group has used the HAT ligand to create molecular squares, in which the magnetic exchange was found to be weak,[6a] and $HAT(CN)_6$ to make a magnetic material, $[CuHAT(CN)_6]_\infty$, that orders as a canted antiferromagnet below 6 K.[7] However, the only report of magnetic exchange mediated by HAT is that of Sletten and co-workers for Cu^{II} chains.[6b]

We previously reported[8] a mixed-ligand material containing dicyanamide and 2,2′-bipyrimidine that showed dimerlike behavior due to strong magnetic exchange through a bis-bidentate bipyrimidine ligand and very weak exchange through the $\mu_{1,5}$-dicyanamide ligands. We anticipated that a similar system incorporating dicyanamide and HAT might reveal trimerlike magnetic properties. The aqueous reaction[9] of excess $CoSO_4$, $Na[N(CN)_2]$, and HAT in a 6:6:1 ratio led to the isolation of red crystals that upon drying had the composition of $Co^{II}_3(HAT)[N(CN)_2]_6(OH_2)_2$ based on elemental analysis, and herein, we report the structure and magnetic properties.

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(9) To a 15 mL aqueous suspension of HAT (43.0 mg; 0.1838 mmol) was added a concentrated aqueous solution of excess $CoSO_4{\cdot}7H_2O$ (309.9 mg; 1.1026 mmol), and after the solution became clear, solid $Na[N(CN)_2]$ (98.2 mg; 1.1026 mmol) was added. The solution was stirred for 2 h at 80 °C, filtered warm, and left to slowly evaporate. After two weeks, small red crystals formed. The crystals lost water of hydration over an extended period of time. All attempts to quantify the amount of water present by thermal gravimetric analysis failed because of sharp water loss at room temperature. Calcd (obsd) for $Co_3(HAT)[N(CN)_2]_6(OH_2)_2$, $Co_3C_{24}N_{24}H_{10}O_2$: C, 34.17 (34.25); H, 1.19 (1.28); N, 39.87 (39.61)%. IR ($\nu_{C\equiv N}$): 2194s, 2164s, and 2133s; 3062w ($\nu_{N\cdots H}$) (hydrogen bonding interactions with unbound water);[8] ~3430 (ν_s and ν_{as}, OH); 1631 cm^{-1} (δ, H_2O). HAT: 1485 s, sp (ν_{CC}), 1389 s, sp (ν_{CN}), 1111 s, sp (δ_{CH}, in-plane), 853 m (δ_{CH}, out-of-plane), 470 s, sp, 419 m, sp (δ_{ring}) cm^{-1}.

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Despite repeated and varied attempts, the largest high quality crystal found was 0.04 × 0.10 × 0.10 mm, which resulted in a very weak data set (av $I/\sigma = 1.87$), and the absence of high-angle data limits the resolution to about 1.2 Å. One of the central CN_{amide} fragments in a $[N(CN)_2]^-$ anion could not be located, although its position is unambiguously defined by the other atoms. The sixth dicyanamide fragment could not be located because of the poor data arising from the small crystal size, large amount of disordered water, and so forth. The crystallographic data were scrutinized for the possibilities that (a) the water molecules bound to Co(1) and Co(2) could be bridging dicyanamides and (b) the highly disordered dicyanamide fragment, [N(61)−C(62)···N(63)], could be two terminally bound and highly disordered dicyanamide anions. The first possibility was ruled out on the basis of typical $Co-N_{nitrile}$ and Co···Co distances in known dicyanamide complexes. The second possibility led to poorer refinement statistics. Thus, the crystallographically determined formula is $[Co^{II}_3(HAT)[N(CN)_2]_5(OH_2)_2]^+$. However, the presence of a sixth $[N(CN)_2]^-$ and divalent Co is supported by the elemental analysis and magnetic data as well as by the need for charge balance. The presence of the sixth dicyanamide as an unbound, highly disordered anion among the water molecules of the void spaces is supported by a $\upsilon_{C\equiv N}$ absorption at 2133 cm^{-1}. For comparison, $[PPh_4][N(CN)_2]$, possessing unbound $[N(CN)_2]^-$, exhibits $\upsilon_{C\equiv N}$ at 2227s, 2188s, and 2130s cm^{-1}, while absorptions for $Na[N(CN)_2]$ possessing $[N(CN)_2]^-$ bound to Na^+ ions occur at 2288s, 2236s, 2228s, and 2181s cm^{-1} (Table S1).

The program SQUEEZE was used to analyze the void spaces in the lattice for water molecules as well as unlocated $[N(CN)_2]^-$ whose presence could not be determined directly. Two void spaces of equal volume (788 Å^3) were located in the unit cell, each containing 246 e^- (corresponding to ca. 24 water molecules) for a void-space count of 492 e^-, or a $[N(CN)_2]^-$ and nine water molecules per asymmetric (formula) unit not directly coordinated to Co. These void spaces correspond to approximately 37% of the total volume of the crystal, although the actual volume must be somewhat less because of the presence of crystallographically unlocated atoms. The occupation of this void space predominantly by unbound water could lead to the classification of this material as microporous, and it is interesting to note that the percentage of void space, 37%, in this material is identical to that found for $[Co(HAT)Cl_2]_4$.[6a]

$Co_3(HAT)[N(CN)_2]_6(OH_2)_2$ is composed of trinuclear Co_3(HAT) groups linked together by dicyanamide ligands (Figure 1). There are two different octahedral Co^{II} centers; Co(3) is coordinated to two N's from HAT and four nitrile N's from two $\mu_{1,5}$-dicyanamides, and Co(1) and Co(2) consisting of two N's from HAT, three N's from two $\mu_{1,5}$-dicyanamides, and one O from a bound water molecule. This corresponds to the formula of $[Co_3(HAT)[N(CN)_2]_5(OH_2)_2]^+$; however, elemental analysis, IR, and charge balance considerations indicate that a sixth dicyanamide anion is present.

The Co^{II}···N distances range from 2.033 to 2.215 Å. The C···N distances and angles of the dicyanamide and HAT ligands are consistent with previously reported structures.[10] The Co_3(HAT) moiety is an approximate equilateral triangle with Co···Co separations of 7.075(6), 7.113(6), and 7.146(6) Å, Figure 1b. Each HAT plane is then capped by a $\mu_{1,5}$-dicyanamide linked Co atom to create a corner sharing tetrahedral network (Figure 2). The Co···Co separations through the μ-dicyanamides are 7.882(6), 7.893(6), and 7.911(6) Å and, hence, are ~0.8 Å longer than the Co···Co separations via the HAT ligand.

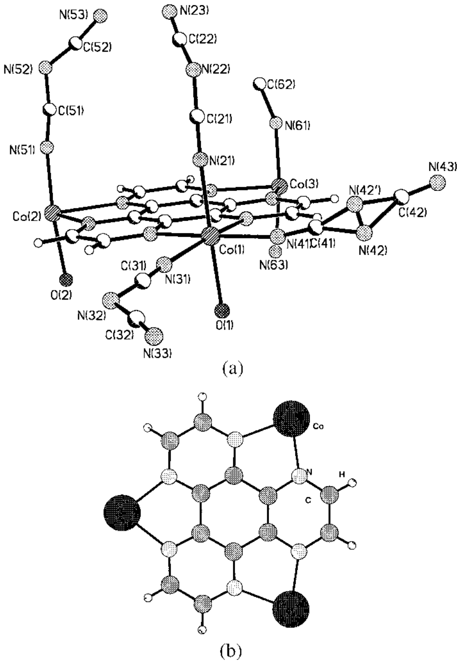

Figure 1. Atom labeling scheme for $[Co_3(HAT)[N(CN)_2]_5(OH_2)_2]^+$ (Å) (a): Co(1)···N(21), 2.059(11), Co(1)···N(31), 2.056(7), Co(1)···N(41), 2.049(8), Co(1)···O(1), 2.119(7), Co(1)···N(2), 2.156(6), Co(1)···N(1), 2.215(7), Co(2)···N(51), 2.050(11), Co(2)···O(2), 2.137(7), Co(2)···N(33), 2.035(7), Co(2)···N(43), 2.066(7), Co(2)···N(3), 2.160(6), Co(2)···N(4), 2.212(7), Co(3)···N(61), 2.033(11), Co(3)···N(23), 2.048(8), Co(3)···N(53), 2.087(8), Co(3)···N(5), 2.181(7), Co(3)···N(6), 2.186(7), and Co(3)···N(63), 2.088 (8), and illustration of the Co_3(HAT) core (b).

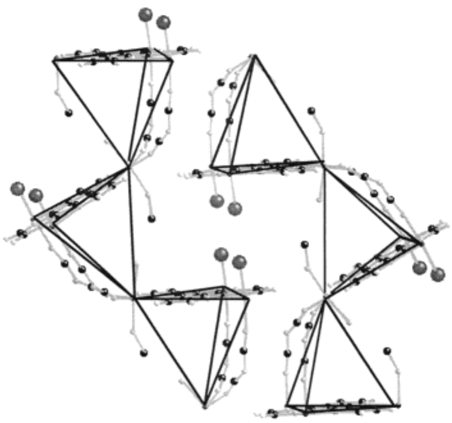

Figure 2. Schematic showing $[Co_3(HAT)[N(CN)_2]_5(OH_2)_2]^+$ with corner sharing tetrahedral network drawn. Average Co···Co separation within the HAT plane is 7.116 Å and between Co_3HAT and the apex is 7.895 Å.

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The reciprocal magnetic susceptibility, $\chi^{-1}(T)$, and $\chi T(T)$ between 2 and 300 K are shown in Figure 3. The room temperature χT value of 5.78 emu K mol^{-1} is consistent with that expected for three isolated $S = {}^3/_2$ spin centers (i.e., 5.63 emu K mol^{-1}). The close agreement between the experimental and expected room temperature $\chi T(T)$ values suggests that there is very little spin−orbit coupling in this system. This observation is corroborated by a poor fit to an equation for $^4T_{1g}$ ions,[11] which accounts for spin−orbit coupling. Instead, the data can be fit by an expression for $S = {}^3/_2$ systems with dominant zero field splitting effects, D,[12] eq 1−4:

$$\chi_{\parallel} = \frac{Ng^2\mu_B^{\ 2}}{k_BT}\,\frac{1 + 9e^{-2D/k_BT}}{4(1 + e^{-2D/k_BT})} \tag{1}$$

$$\chi_{\perp} = \frac{Ng^2\mu_B^{\ 2}}{k_BT}\,\frac{4 + (3k_BT/D)(1 - e^{-2D/k_BT})}{4(1 + e^{-2D/k_BT})} \tag{2}$$

$$\chi' = \frac{\chi_{\parallel} + 2\chi_{\perp}}{3} \tag{3}$$

$$\chi = \frac{\chi'}{1 - \left(\dfrac{2zJ}{Ng^2\mu_B^{\ 2}}\right)\chi'} \tag{4}$$

where N is Avogadro's number, μ_B, the Bohr Magneton, k_B, Boltzmann's constant, g, the Lande g value, and D, the zero field splitting, with $g = 2.01$ and $D = 38.9$ cm^{-1}. There are surprisingly few quantitative reports of D in octahedral Co^{II} complexes. However, $D = 82.7$ cm^{-1} was found for the highly tetragonally distorted six-coordinate complex Co(acac)$_2$(H$_2$O)$_2$ (acac = acetylacetonate),[13] while $D = 53$ cm^{-1} was observed for Co(pyridine-N-oxide)$_6$[ClO$_4$]$_2$, which exhibits a slight (crystallographically unobservable) trigonal distortion.[14] In the present system, Co(1) and Co(2) are highly trigonally distorted, and Co(3) contains two bonds, from N$_{HAT}$, that are elongated relative to the other four Co(3)−N$_{[N(CN_3)]^-}$ bonds. If we consider the D in the present system as an average of two trigonally distorted metal centers ($D = 53$ cm^{-1}) and one psuedotetrahedral metal center ($D = -36$ to $+13$ cm^{-1}),[14a] D should range from 23.3 to 39.7 cm^{-1} in accord with observation. A molecular field approximation, eq 4, showed negligible intermolecular, zJ, interactions.[15]

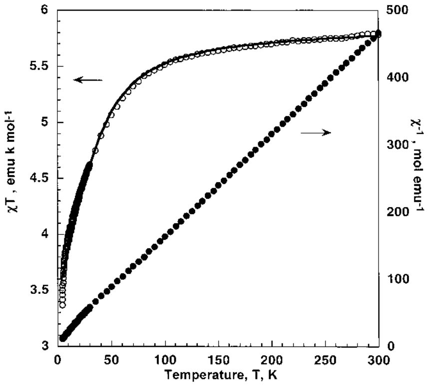

Figure 3. Temperature dependence of χ^{-1} (●) and χT (○) for Co$_3$(HAT)[N(CN)$_2$]$_6$(OH$_2$)$_2$. Solid line represents fit to eq 3 with $g = 2.01$ and $D = 38.9$ cm^{-1}.

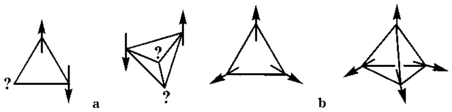

Figure 4. Schematic showing (a) spin frustration in triangular and tetrahedral arrays and (b) the compromise spin states adopted by triangular and tetrahedral arrays.

From a consideration of the structural framework, geometrically induced spin frustration is expected for triangular and tetrahedral arrays in which the spin bearing centers would like to couple antiferromagnetically.[16] Figure 4a shows how one or more spin centers will be unable to satisfy the criteria for antiferromagnetic coupling.

To overcome this frustration, materials will often undergo a transition from a paramagnetic state to a noncollinear or compromise spin configuration (Figure 4b). When the unpaired electrons are aligned at 120° and 109° in the triangular and tetrahedral units, respectively, the overall spin vector is equal to zero as is required for antiferromagnetic coupling. Attempts to note the spin frustration via ac magnetic susceptibility and heat capacity measurements failed to reveal a magnetic phase transition down to 2 K.

Co$_3$(HAT)[N(CN)$_2$]$_6$(OH$_2$)$_2$ is a material with a large (~37%) total void fraction and a unique structural motif. The structural motif consists of a corner sharing tetrahedral network ideal for spin frustration. However, the transition to a noncollinear or compromise spin state does not occur down above 2 K, and the magnetic data can be fit to an $S = {}^3/_2$ model for systems dominated by zero-field splitting effects with $g = 2.01$ and $D = 38.9$ cm^{-1}.

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Supporting Information Available: Stretching frequencies ($\nu_{C\equiv N}$) of dicyanamide reference compounds (Table S1), and the crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(16) For a recent review see: Greedan, J. E. *J. Mater. Chem.* **2001**, *11*, 37.