Tetraacetylethane Dianion (Tae) As a Bridging Ligand for Molecular Square Complexes: $Co^{II}_4(Tae)_4(Dpa)_4$, Dpa = Di-2-pyridylamine, a Chiral Molecular Square in the Solid State

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Cyclic tetranuclear metal complexes with ~90° angles at the corners (molecular squares or molecular boxes) are of great current interest.[1−3] The commonly employed strategy for the synthesis of molecular square or box compounds is the self-assembly of the metal ions with appropriate bridging and chelating or multidentate ligands.[1,2] Puddephatt and co-workers have demonstrated recently that one can also construct a molecular box in a controlled fashion by using bridging ligands and pre-assembled dinuclear units.[3] The most interesting and challenging task is the assembly of cyclic chiral molecular arrays such as squares or boxes because of their potential applications in chiral molecular recognition.[2e−g] Stang and co-workers have explored the syntheses of chiral Pt^{II}_4 or Pd^{II}_4 molecular squares by using either chiral chelating ligands such as BINAP or bridging ligands such as 2,6-diazaanthracene, which does not have a rotational symmetry along the M−L−M linkage.[2e] We have been investigating the assembly of chiral molecular complexes involving octahedral metal ions such as Co(II) and Mn(II). Unlike the square-planar Pt(II) or Pd(II) complexes, octahedral Co(II) or Mn(II) complexes with chelating ligands are inherently chiral.[4] Therefore, no chiral auxiliary ligands are required. In addition, the first row transition metal ions such as Co(II) and Mn(II) have interesting magnetic and redox properties which make the molecular square complexes more attractive.[5] Using inherently chiral transition metal complexes as building blocks in the synthesis of chiral, supramolecular complexes has been explored by Stang and co-workers.[2g] The bridging ligand we chose to use is the tetraacetylethylene dianion (tae). The free tae ligand[6] has D_{2d} symmetry. Upon coordinating to octahedral metal ions bound by chelating ligands, the D_{2d} symmetry is reduced to pure rotational symmetries, depending on the chelating ligands. We have demonstrated recently that the tae ligand can bridge two ML_2 units (M = Cu^{II}, Co^{II}, L = a bidentate ligand) to form a helical dinuclear complex with a D_2 symmetry.[7] The chelating ligand we chose to use is the di-2-pyridylamine (dpa) ligand. The dpa ligand not only chelates to a metal ion, thus acting as a terminating ligand to prevent the formation of polymeric species, but also can form intermolecular hydrogen bonds through the noncoordinating amino group, thus facilitating the possible formation of an extended hydrogen-bonded structure.[7] We report herein a novel Co(II) molecular square complex that exhibits a chiral molecular structure in the solid state, obtained by using tae and dpa as the bridging and chelating ligand, respectively.

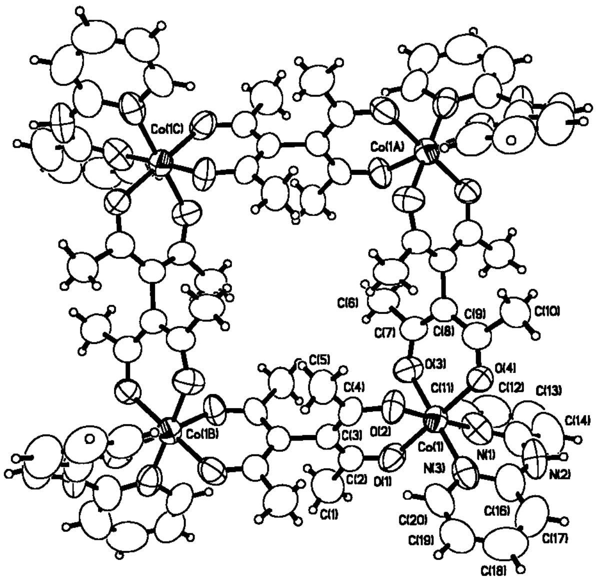

Figure 1. A diagram showing the molecular structure of **1** with 50% thermal ellipsoids and labeling scheme. Selected bond lengths (Å) and angles (deg): Co(1)−O(1) = 1.935(4), Co(1)−O(2) = 1.958(4), Co(1)−O(3) = 1.952(4), Co(1)−O(4) = 1.944(4), Co(1)−N(1) = 1.996(6), Co(1)−N(3) = 2.015(6), C(3)−C(3A) = 1.482(11), C(8)−C(8A) = 1.512(10); O(1)−Co(1)−O(4) = 179.4(2), O(2)−Co(1)−N(1) = 177.9(2), O(3)−Co(1)−N(3) = 178.7(2).

The reaction of $Co(O_2CCH_3)_2(H_2O)_4$ with di-2-pyridylamine (dpa) and tetraacetylethane in a 1:1:1 ratio in a mixed solvent of CH_2Cl_2 and methanol at 23 °C produced the dark brown microcrystalline compound, $Co^{II}_4(tae)_4(dpa)_4$ (**1**), in ~15% yield, along with $Co_3(O_2CCH_3)_4(dpa)_2$[7a] and an insoluble yellow brown solid that has not been fully characterized yet. The structure of compound **1** was determined by a single-crystal X-ray diffraction

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(8) Crystal data for **1**: $a = 15.2342(7)$ Å, $b = 15.6511(7)$ Å, $c = 22.0915(10)$ Å, $V = 5267.3(4)$ Å^3, $Z = 2$ (for the formula of $Co_4(dpa)_4(tae)_4/(HO_2CCH_3)_2(CH_2Cl_2)_4(H_2O)$, orthorhombic, *I*222. Data were collected over the 2θ range of 3.18−57.56° at 23 °C on a Siemens CCD X-ray diffractometer with Mo Kα radiation. Data were processed on a pentium PC with a Siemens SHELXTL software package (5.0). Convergence to the final *R* values of $R_1 = 0.0779$, $wR_2 = 0.1814$ ($I > 2\sigma(I)$ and $R_1 = 0.1211$, $wR_2 = 0.2194$ (all data) for **1** were achieved by using 6830 reflections and 294 parameters. The details of X-ray crystallographic analyses are given in the Supporting Information. Anal. Calcd for $Co_4(dpa)_4(tae)_4/(HO_2CCH_3)_2{\cdot}(CH_2Cl_2)_4{\cdot}H_2O$ $C_{88}H_{102}Co_4Cl_8O_{21}N_{12}$: C, 48.41; H, 4.68; N, 7.70. Found: C, 48.27; H, 4.51; N, 7.91.

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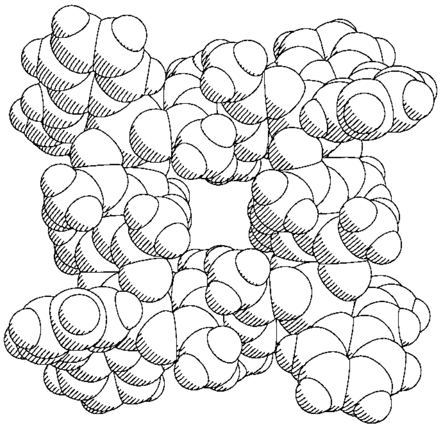

Figure 2. A space-filling diagram showing the helical edges and the cavity of the molecular square.

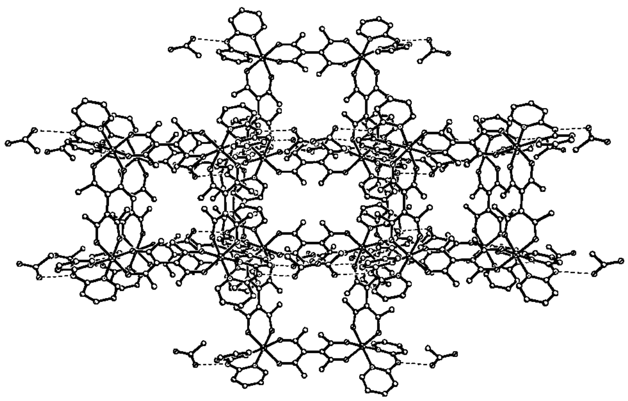

Figure 3. A packing diagram showing the stacking of **1** and the hydrogen bound acetic acid molecules.

analysis with a Siemens CCD X-ray diffractometer.[8] Compound **1** crystallizes in the chiral space group *I*222. As shown in Figure 1, compound **1** has a crystallographically imposed D_2 symmetry with one-quarter of the molecule being in the asymmetric unit. As a consequence of the D_2 symmetry, the four Co(II) centers have the identical chirality, i.e., either all Δ or all Λ optical geometry. Compound **1** is therefore a chiral molecular square in the solid state. Each edge of the square, i.e., each pair of Co_2, has a helical structure similar to that observed in $[Co_2(tae)(dpa)_4][(O_2CCH_3)_2(H_2O)_2]$.[7b] The overall structure of **1** could be therefore described as a cyclic helicate (Figure 2). The Co(II) ions in **1** have a typical octahedral coordination geometry. The tae ligand bridges two Co(II) ions in a similar fashion as that observed in the dinuclear complex $[Co_2(tae)(dpa)_4][(O_2CCH_3)_2(H_2O)_2]$.[7] The twisting angle between the two diketone portions of the tae ligand is 88.0°, similar to that observed in the cobalt dimer compound.[7] The Co−Co separation distances along the edge of the square are essentially identical (8.009(5) and 8.000(5) Å) while the diagonal Co−Co separation distance is 11.306(6) Å. The shortest distance between the hydrogen atoms of the opposite methyl groups inside the square is about 4.2 Å. The size of the cavity in the molecular square is therefore about 4.2 × 4.2 Å. The dpa ligand is chelated to the Co(II) ion via the two pyridyl nitrogen atoms. There are two acetic acid and two water molecules per molecule of **1** in the crystal lattice as established by X-ray diffraction. Both acetic acid and water molecules are disordered over two symmetry-related sites and appear to be hydrogen bonded to each other. Due to the disorder, the pattern of hydrogen bonds between the acidic acid and water molecules could not be established conclusively. The X-ray data show, however, unambiguously that the acetic acid molecule forms a hydrogen bond with the uncoordinated amino group of the dpa ligand as indicated by the N(2)−O(6) distance of 2.80(1) Å (Figure 3). The molecular squares are therefore likely linked together via hydrogen bonds between the acetic acid, H_2O, and the dpa ligand to form an extended array, but it could not be conclusively established by X-ray data available at this time.

Although each individual crystal of **1** consists of one enantiomer only, the bulk of the crystals are believed to be a racemate. The solution of compound **1** in CH_2Cl_2 exhibits an essentially zero optical rotation, an indication that compound **1** is indeed a racemate in solution. The problem of whether the enantiomer of **1** undergoes racemization in solution could not be solved at this time because the individual chiral crystals of **1** are too small to allow any meaningful kinetic study. Attempts to selectively crystallize one enantiomer by replacing the hydrogen-bound acetic acid molecule with an optically pure (*s*)-(+)-2-methylbuyric acid were unsuccessful.

The nearly 90° twisting of the tae ligand results in the orthogonality of d orbitals from two neighboring Co(II) ions, which could be in favor of ferromagnetic exchanges.[9] We therefore examined the magnetic properties of **1** by the measurement of magnetic susceptibility versus temperature at 5−300 K. Compound **1** has a magnetic moment of 8.30 μ_B at 300 K, which increases gradually with the decrease of temperature and reaches the maximum of 10.35 μ_B at 65 K, indicative of the presence of ferromagnetic exchanges (the magnetic moment for four noninteracting Co(II) ions is ∼8.0 μ_B). At temperatures below 65 K, the magnetic moment decreases slowly and reaches 9.58 μ_B at 5 K. The behavior of compound **1** is similar to that of $[Co_2(tae)(dpa)_4][(O_2CCH_3)_2(H_2O)_2]$, where weak ferromagnetic exchanges dominate in the 60−300 K temperature range.[7]

Compound **1** is a rare example of structurally characterized molecular squares with a chiral structure in the solid state. It demonstrates that ligands which have a ∼90° twist, such as the tetraacetylethylene dianion, can facilitate the formation of chiral structures, e.g. molecular squares, where octahedral metal ions are employed. In addition, compound **1** also further demonstrates that the tae ligand can facilitate ferromagnetic exchanges between the metal centers. Further investigation on the utility of ligands such as tae in the assembly of chiral macrocyclic metal complexes and the chemical and physical properties of the complexes is being conducted in our laboratory.

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Supporting Information Available: Tables of crystallographic analysis, atomic coordinates and isotropic thermal parameters, a complete list of bond lengths and angles, anisotropic thermal parameters, hydrogen parameters for **1**, and diagrams of $[Co_2(tae)(dpa)_4][(O_2CCH_3)_2(H_2O)_2]$[7b] (9 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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