Inorg. Chem. **2005**, 44, 486–488

Inorganic Chemistry

Communication

Heterometallic Metal–Organic Frameworks Based on Tris(dipyrrinato) Coordination Complexes

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Received December 6, 2004

A novel class of heterometallic metal–organic frameworks (MOFs) has been synthesized and characterized. The MOFs rely on the use of tris(dipyrrinato) coordination complexes as the bridging structure and silver(I) ions as the linking unit. The building blocks and resulting MOFs have been structurally characterized by using single-crystal X-ray diffraction. The modular nature of this approach is demonstrated by the use of both iron(III) and cobalt(III) complexes. The MOFs have strong electronic absorption features originating from the metal–dipyrrin chromophore and have continuous channels throughout the lattice that are occupied by ordered and disordered solvent molecules.

The design of extended solids has become a field of significant interest in supramolecular chemistry. These compounds hold promise as new materials with novel catalytic, magnetic, electronic, and optical properties.[1−4] In addition, the use of porous materials for uptake, storage, and release of small molecules has been a major focus of study. Extended solids, particularly those held together by metal−ligand bonds, have been constructed with the hope that judicious ligand design can allow for the predictable synthesis of a given extended framework. Among the many available examples, the Ag(I)−N donor atom networks of Lee and Moore are an excellent illustration of these efforts.[5−9] These groups have described several extended solids composed of nitrogenous donor ligands in combination with a variety of silver(I) salts. The bridging ligands are typically rigid, polytopic 3-fold symmetric linking units containing cyanophenyl or pyridyl groups. On the basis of this approach, a novel strategy to construct heterometallic metal−organic frameworks (MOFs)[10−14] using coordination complexes as building blocks is presented. Both Co/Ag and Fe/Ag heterometallic network solids have been synthesized and characterized.

Coordination complexes or "metalloligands" have been touted as a promising route to preparing functional MOFs. Recent approaches using coordination complexes have focused on sophisticated polydentate or macrocyclic ligands where the encapsulated metal ion plays a limited role in organizing the geometry of the monomeric unit.[15−18] In contrast, the strategy described here uses a transition metal ion to assemble simple ditopic ligands into a coordination complex that can serve as a high symmetry building block for MOFs. This approach is extremely modular as the use of different metal ions will afford metalloligands with different geometries and spectroscopic characteristics, which can give rise to extended solids with a variety of structures and physical properties. Furthermore, the use of octahedral tris(chelate) complexes affords the opportunity to exploit the handedness of these compounds to obtain homochiral extended solids.

Transition metal complexes with ditopic dipyrromethene (dipyrrin) ligands were chosen to reproduce the 3-fold

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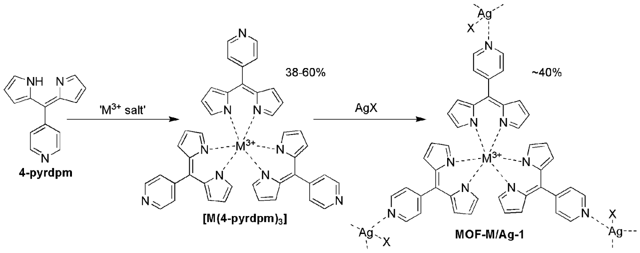
10.1021/ic048289z CCC: $30.25

Scheme 1. Synthesis of Heterometallic Frameworks MOF-M/Ag-1

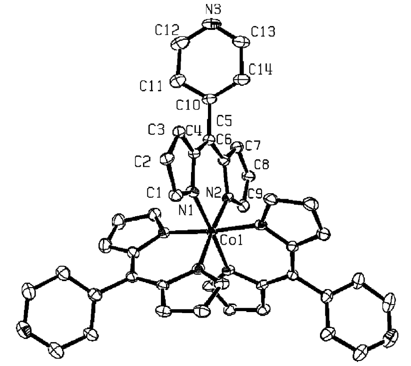


symmetry of the ligands used in earlier MOF syntheses (Scheme 1).[5−9] Dipyrrin complexes are stable, have rich electronic absorption spectra, and can be isolated by using conventional flash chromatography. The geometry of the resulting complexes allows for the introduction of a second ligating site with a definite directionality, making suitable monomers for preparing extended structures.[19−23] A pyridyl functionalized dipyrrin was synthesized as previously described[22,23] and combined with the appropriate metal salt to obtain the desired building blocks [Co(4-pyrdpm)$_3$] and [Fe(4-pyrdpm)$_3$] (4-pyrdpm = 5-(4-pyridyl)-4,6-dipyrrinato) in modest yields.

[Co(4-pyrdpm)$_3$] and [Fe(4-pyrdpm)$_3$] are neutral, air and moisture stable, highly colored complexes with intense electronic absorption features characteristic of these compounds.[19−21] Both complexes have been characterized by single-crystal X-ray diffraction studies, and the molecular structure of each is shown in Figure 1. The essentially isostructural complexes have a distorted octahedral coordination geometry (Co−N ~1.94 Å, Fe−N ~1.96 Å). As anticipated, the three pyridyl moieties are poised in a pseudo-3-fold symmetric fashion pointing away from the tris(chelate) metal center.

To obtain the desired MOF, the discrete coordination compound [Co(4-pyrdpm)$_3$] was combined with 1 equiv of AgOTf (OTf = trifluoromethanesulfonate, triflate) in benzene solution at concentrations ranging from ~0.2 to 1.3 mM. The mixture immediately generated a red precipitate that was dissolved by dilution with acetonitrile (see Supporting Information). The mixtures were shielded from light, and upon slow evaporation, the solutions generated large, orange crystals after 1−2 weeks. The bright orange color of the crystals was indicative of the [Co(4-pyrdpm)$_3$] core; this was confirmed by the diffuse reflectance UV−vis spectrum of these crystals, which showed an absorption feature centered at 557 nm with another broad, intense absorption at >610 nm. Similar spectral features are found in the [Co(4-pyrdpm)$_3$] monomer complex (Figure S1). In addition, IR spectra of the crystals had several features indicative of the dipyrrin complex (1380, 1346, 1021, 995 cm^{-1}).[23]

A single-crystal X-ray diffraction study of the orange crystals revealed the formation of a heterometallic MOF (Figure 2). The material crystallized in the orthorhombic space group *Pbcn*, with the [Co(4-pyrdpm)$_3$] complexes linked together via the pyridyl nitrogen atoms to silver(I) centers. Each silver(I) ion is bound by three pyridyl groups and one triflate counterion, in a distorted trigonal pyramidal coordination geometry. The triflate anion binds to the apical position of the coordination sphere with a Ag−O bond length of 2.57 Å. The average Ag−N bond length of 2.24 Å is comparable to those found in other extended solids based on organic building blocks. The cobalt(III) coordination sphere maintains the octahedral geometry found in the



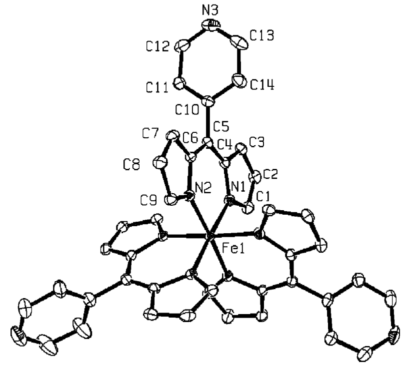


Figure 1. Structural diagram of [Co(4-pyrdpm)$_3$] (top) and [Fe(4-pyrdpm)$_3$] (bottom) with partial atom numbering schemes (ORTEP, 50% probability ellipsoids). Hydrogen atoms and solvent have been omitted for clarity.

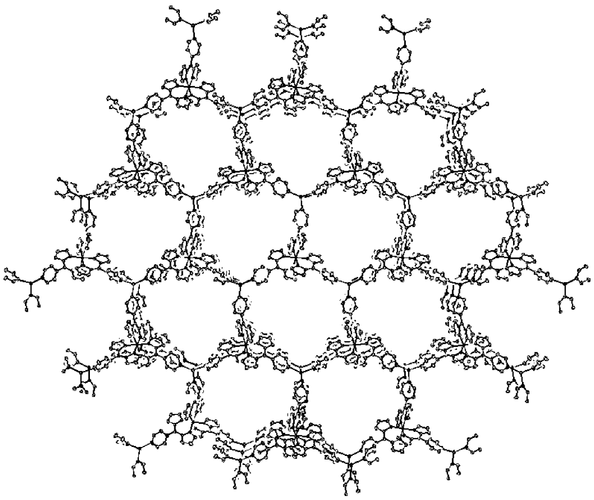


Figure 2. ORTEP representation (50% probability ellipsoids) of the packing in MOF-Co/Ag-1 viewed down the crystallographic *b*-axis. Only one of two interpenetrated networks is shown in order to highlight the connectivity the lattice. Solvent molecules, hydrogen atoms, and counterions have been omitted for clarity.

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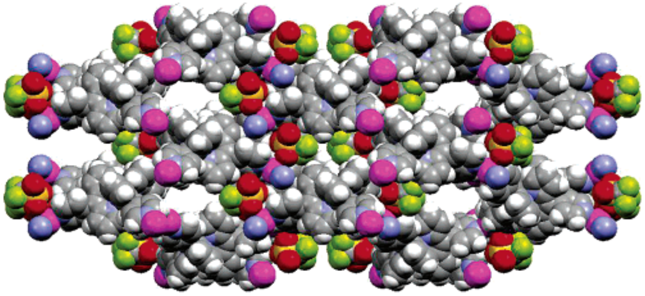

Figure 3. Space-filling representation of the packing in MOF-Co/Ag-1 viewed down the crystallographic *c*-axis. Rounded channels can be seen through the MOF structure. Solvent molecules have been omitted for clarity.

monomeric structure, creating a 3-fold symmetric center as anticipated. The Co−N bond lengths (Co−N ~1.94 Å) are unchanged from the [Co(4-pyrdpm)$_3$] starting material, and the Co−Ag distance is ~9.78 Å. It is important to note that the synthetic method used to obtain this MOF is essentially identical to the previously described procedures used with organic ligand systems.[6−9] This mitigates the need for identifying new synthetic procedures for these materials and demonstrates that these symmetric coordination compounds can directly substitute for the related organic ligands.

The extended solid is composed of two interpenetrated [Co(4-pyrdpm)$_3$]···Ag networks. Each network contains both Δ and Λ isomers of the octahedral cobalt(III) centers; hence, the structure is not homochiral. The resulting lattice has oval-shaped channels that are clearly seen when viewed down the crystallographic *c*-axis (Figure 3). Within the channels, two cocrystallized molecules of acetonitrile were identified in the X-ray structure determination. In addition, a substantial amount of residual electron density was found in the oval-shaped channels of the structure; presumably, this electron density arises from disordered solvent molecules often found in MOF structures.[1] These solvent-accessible channels were evaluated by using the program SOLV included in the PLATON software package.[24] The calculation, performed on only the framework structure and the triflate counterions, generated a free volume of ~4426 Å^3. This corresponds to 39% of the total cell volume.

An isostructural MOF was obtained by an identical procedure by using [Fe(4-pyrdpm)$_3$] and AgBF$_4$ as the monomeric units. MOF-Fe/Ag-1 is essentially isomorphous with MOF-Co/Ag-1 (see Supporting Information), with the BF$_4$ anions residing near the silver(I) ions (Ag−F distance 2.68 Å) and an Fe−Ag distance of ~9.79 Å. This material also showed open channels along the *c*-axis with a calculated free volume of ~4680 Å^3 (42% of total cell volume). The synthesis of MOF-Fe/Ag-1 demonstrates the modular nature of the synthetic strategy presented here, clearly showing that the tris(chelate) metal ion can be changed to modify the physical properties of these MOFs.

In summary, we report a new strategy for the synthesis of heterometallic MOFs, whereby coordination complexes are used as the monomeric building blocks. These monomers are connected together using silver(I) ions in a fashion that parallels those reported for geometrically related organic ligands. The use of an octahedral tris(chelate) metalloligand demonstrates the ability to augment the properties of the MOF, in this case with strong optical absorbance features from the metal(III)−dipyrrinato chromophore. The physical properties can be tuned in a modular fashion by simply changing the metal ion used to form the monomeric building block. The results presented bode well for the prospect of incorporating magnetic or fluorescent properties,[25] as well as the preparation of homochiral MOFs based on this strategy. Detailed studies on the stability, solvent exchange properties, and host−guest chemistry of MOF-Co/Ag-1, MOF-Fe/Ag-1, and related MOFs are underway.

Acknowledgment. We thank Prof. Arnold L. Rheingold and Dr. Lev N. Zakharov (U.C.S.D.) for help with the X-ray structure determinations. This work was supported by the University of California, San Diego, a Chris and Warren Hellman Faculty Scholar award, and the donors of the American Chemical Society Petroleum Research Fund. This material is based upon work supported under a National Science Foundation Graduate Research Fellowship (S.R.H.). S.M.C. is a Cottrell Scholar of the Research Corporation.

Supporting Information Available: Figures S1−S4. Experimental details for syntheses, spectroscopic studies, and X-ray structures. Crystallographic data in CIF format. This material is also available free of charge via the Internet at http://pubs.acs.org. X-ray crystallographic files in CIF format are available free of charge via the Internet at http://www.ccdc.cam.ac.uk. Refer to CCDC reference numbers 251126, 251127, 251128, and 251129.

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