Dynamer and Metallodynamer Interconversion: An Alternative View to Metal Ion Complexation

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ABSTRACT: A bifunctional molecule containing both a bidentate binding site for metal ions and an aminopyrimidine H-bond donor-acceptor site has been synthesized, and its properties, in its free and coordinated forms, have been established in solution and in the solid state by analytical and spectroscopic methods as well as by X-ray structure determinations. Structural characterization has shown that it forms a one-dimensional H-bonded polymeric assembly in the solid state, while spectroscopic measurements indicate that it also aggregates in solution. The reaction of a simple Fe(II) salt with this assembly results in the emergence of two geometrical isomers of the complex: $[FeL_3](BF4)_2 \cdot 9H_2O$ —C1 (meridional, *mer*) and $[FeL_3]_2(SiF_6)(BF_4)_2 \cdot 12H_2O$ —C2 (facial, *fac*). While, complex C1 in the solid state generates a one-dimensional H-bonded polymer involving just two ligands on each Fe center, with the chirality of the complex units alternating along the polymer chain, the structure of complex C2 shows NH…N interactions seen in both the ligand and *mer* complex (C1) structures to be completely absent. Physicochemical properties of the free and complexed ligand differ substantially.



INTRODUCTION

Stimuli-responsive architectures that are capable of adapting to changes in their environment via application of chemical or physical stimuli have attracted significant attention. In this context, the study of coordination polymers (CPs) and metal organic frameworks (MOFs) has become one of the most prolific research fields of supramolecular chemistry and crystal engineering over the past few decades.¹ Although full consensus is lacking on their exact definition,² IUPAC classifies CPs as a larger family of materials than MOFs and has defined a CP as a coordination compound with repeating coordination entities extending in one, two, or three dimensions and a MOF as a coordination network with organic ligands containing potential voids.² The design of CPs and MOFs requires careful consideration not only of factors such as the desired properties to be introduced by the metal ion, the nature and relative disposition of the donor atoms of the ligand, and the degree of flexibility of the ligand framework but also of the weak interactions which may arise within the lattice and the stereochemistry of the metal ion centers.³ As a type of weak interaction in metal complex lattices, H-bonding is rather frequently observed, but the deliberate introduction of Hbonding sites as part of the ligand design is still very rare.⁴ Similarly, the chirality of a metal ion center is often recognized but less frequently deliberately exploited.^{4b,5} To further explore both these influences, we have synthesized the ligand L containing a well-known bidentate binding site for metal ions as well as a H-bond donor-acceptor site and have used it to

prepare both organic and inversion stable, chiral metalorganic hydrogen bonding assemblies with distincly different crystal structures and physicochemical properties, for example, carbon dioxide sorption.

One of the applications most often envisaged for porous CPs and MOFs is the storage of carbon dioxide as a potential solution to its greenhouse gas effects. Environmentally friendly and economically viable separation, capture, and storage of greenhouse gases will be increasingly important in the near future.⁶ Both CPs and MOFs represent real possibilities for these applications and can be seen as providing a potential technological breakthrough. Porous CP and MOF design offers quasi-infinite possible combinations, intriguing network topology, structural flexibility, tunable pore size and multiple functionality because the structures and chemical composition can be easily tuned, both by playing on the nature and by coordination of the metal ions and functionalization of the organic linker in the ligands.⁷ One way to give flexibility is to exploit weak interactions like H-bonding or dispersion forces between large aromatic ligands along with the directional covalent bond.^{6a,7b} There is growing interest in the insertion of



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different functional groups such as $-NH_2$, -OH, $-CO_2H$, $-CF_3$, $-SO_3H$, and $-NO_2$ into a CP/MOF structure to improve CO₂ capture or separation.^{6a,8} A positive effect of the introduction of a free amino group on CO₂ binding has been found in a number of different MOFs.^{7a}

We hypothesized that supramolecular assemblies of organic and metal-organic types based on the one bifunctional molecule could behave as systems exhibiting different porous morphology and as a consequence distinct CO_2 sorption properties, the second system being tunable on the basis of the choice of metal ion. The present work represents an exploration of this hypothesis.

RESULTS AND DISCUSSION

Ligand Synthesis. The ligand L, $5 \cdot ([2,2'-bipyridin]-5-yl)$ pyrimidin-2-amine, contains both bipyridine and aminopyrimidine units in its structure (Figure 1). Such a ligand design was thus expected to provide one site for strong metal ion binding (marked red) and one for strong donor-acceptor H-bonding (marked blue).



Figure 1. Generation of H-bond organic and metal-organic polymers.

The synthesis of L is outlined in Figure 2, and the first three steps follow literature methods, with some modifications, starting from the commercially available 2-bromopyridine.⁹ The compound 4 thus obtained was employed in a Stille coupling with 2-amino-5-bromopyrimidine providing the desired product in 50% yield (see Experimental Section for details). A satisfactory yield was obtained without protection of the amino group, enabling the two steps of protection/ deprotection to be avoided. The isolated lustrous, white solid ligand L was found to be poorly soluble in acetonitrile, while it



Figure 2. Synthesis of ligand **L**. Metal coordination site is marked by red; the hydrogen bonding site is marked by blue.

showed good solubility in polar solvents like DMSO and DMF and in chlorinated solvents like CHCl₃ and TCE (1,1,2,2tetrachloroethane). Confirmation of the expected structure of L was provided by solution NMR measurements (¹H, ¹³C NMR, ¹H–¹H COSY NMR, ¹H–¹³C HSQC NMR), IR spectroscopy, and mass spectroscopy (see SI for details, Figures S7–S14). The form of the ligand in the solid state was also established by a single crystal X-ray structure determination (see below).

Ligand Properties. In Solution. Solution ¹H NMR spectra were recorded in d_2 -TCE as a solvent having weak H-bond donor or acceptor properties and in d_6 -DMSO as a good Hbond acceptor, which would be expected to prevent any selfaggregation of L. TCE was also used because its wide liquid range (-44 to 146 °C) renders it suitable for variable temperature measurements. The room-temperature spectra in the two solvents were clearly different, with the most obvious difference being the displacement of the NH proton resonance from near δ 7 in d_6 -DMSO (Figure 3a) to near δ 5 in d_2 -TCE (Figure 3b) and the broadening of the NMR resonance lines in d_2 -TCE in contrast to the sharp spectrum in d_6 -DMSO. While the NH proton signals are not the only ones to undergo shifting due to the change of solvent, their shifts are by far the greatest. This we interpret as evidence that in d_2 -TCE the ligand is involved in dynamic self-aggregation through intermolecular N-H-N bonding between the ligands (as observed in the solid state—see below), while in d_6 -DMSO the NH protons strongly interact with the solvent itself, resulting in a more pronounced shifts toward a lower field. On adding d_6 -DMSO to the d_2 -TCE solution of the ligand L, the NH resonance shifted markedly downfield, as a consequence of the disruption of the ligand-ligand hydrogen bonding network by solvent molecules and formation of new hydrogen bonds of type L-DMSO (Figure 3c). Other, less pronounced shifts of the proton signals might well be due to weak H-bonding interactions but also to electronic charge redistributions induced by the strong NH interactions, as well as ring current effects in any aggregated species.

The room temperature formation of a hydrogen bonded assembly of L in TCE was also confirmed by dynamic light scattering measurements (Figure S20). These indicated the presence of large supramolecular aggregates over a wide range of sizes but with an average radius of 1078 nm. The relatively high polydispersity index (0.639) may indicate that aggregates of various rather different forms were present.



Figure 3. ¹H NMR (600 MHz) spectra at ambient temperature of ligand L (concentration: 1.5×10^{-3} M). Recorded in (a) DMSO- d_{6} , (b) TCE- d_{2} , (c) TCE- d_{2} with the addition of DMSO- d_{6} .

These data were further confirmed by scanning electron microscopy (SEM), where three-dimensional rod-shaped architectures of sizes $(1 \ \mu m)$ similar to those estimated for the solution were obtained by evaporating the TCE solution of the ligand on silica (see SI, Figure S21). Since H bonds are expected to be disrupted by an increase in temperature, VT ¹H NMR measurements (Figure 4a) were performed with a d_2 -TCE solution of L. Over a 90° range (243–333 K), the spectrum showed negligible change in form, but small shifts, both up- and downfield, were observed for some signals.

The most diagnostic signal comes from the NH₂ group, which must be directly involved in the formation of any hydrogen-bonded network. The temperature coefficient ($\Delta\delta$ / ΔT) of the NH signal chemical shift (Figure S22) is commonly used¹⁰ as a criterion of the presence and strength of H-bonds and here has a value of -1.43 ppb K^{-1} consistent with the presence of strong hydrogen bonds. The downfield shift of the NH resonance (marked blue) on decreasing the temperature was consistent with H-bond formation, although the spectra provided no evidence of any dramatic change in speciation. Since an associative equilibrium in solution should be concentration dependent and the VT ¹H NMR measurements were performed at a relatively high concentration (1.5×10^{-3}) M), it was decided to use spectrophotometry to carry out measurements at a much lower concentration $(5 \times 10^{-5} \text{ M})$ by recording the electronic absorption spectrum as a function of temperature (Figure 4b). As the temperature was lowered, a new band in the vicinity of 350 nm appeared. At the concentration used, large aggregates would presumably not be present, and the apparent isosbestic point indicates that simpler H-bond supramolecular species may have been in equilibrium. Nonetheless, the changes with temperature appear to be quite substantial. As the aminopyrimidine unit is a

divergent, ditopic H-bonding entity, it can be involved in stepwise association up to the formation of polymers, and a quantitative analysis of the equilibria involved could well be complicated, depending strongly on the solvent, and the present measurements can only be interpreted as evidence that some degree of aggregation occurs over a wide concentration range in TCE.

In the Solid State. Crystals of L suitable for X-ray diffraction measurements were obtained by slow evaporation of a chloroform solution.

The ligand deposited as colorless, monoclinic needles, space group $P2_1/n$, with a single molecule making up the asymmetric unit. Crystal and structure refinement data are given in Table S1 (see Supporting Information for details), and the molecule, with atom numbering, is shown in Figure 5a. Viewed down c, the lattice has a herringbone array of the molecules (Figure 5b), a form frequently observed with both aromatic and heteroaromatic species.¹¹ In the present case, analysis of the Hirshfeld surface¹² obtained using CrystalExplorer¹³ shows that both NH N and CH N interactions between molecules exceed dispersion. Pairs of reciprocal NH…N and N…HN interactions (N2…H1A 2.16 Å; N3…H1B 2.27 Å) of a given molecule with its neighbors are unsymmetrical (Figure 5c) but give rise to double-stranded H-bond polymer units which are cross-linked by CH…N interactions (H12…N5 2.56 Å) to give the lattice its three-dimensional structure. The trigonal form of the amino-N and the blockage of both pyrimidine-N sites by the H-bonding indicate that any interaction of CO₂ with the amino-pyrimidine units in the solid would be inhibited, but of course the pyridine-N not involved in N…HC interaction could act, even if weakly, as a site for zwitterionic carbamatoderivative formation.



Figure 4. Thermodynamic stability of the structure based on hydrogen bonds in TCE. (a) VT NMR (600 MHz TCE- d_2) spectra of ligand L, 1.5 × 10⁻³ M. (b) Variable temperature UV-vis spectra recorded during cooling of a TCE solution of ligand L, 5 × 10⁻⁵ M, T = 373-283 K.

Complex Ion Syntheses and Characterization. Syntheses. Ligand L and $[Fe(OH_2)_6](BF_4)_2$ react rapidly in a 3:1 molar ratio in acetonitrile to give a deep purple solution from which violet crystals of $[FeL_3](BF_4)_2 \cdot 9H_2O$ —C1 deposit (see Experimental Section for spectroscopic data). The crystals are of low solubility in chlorinated solvents (DCM, TCE) but dissolve readily in DMF, DMSO, MeCN, and H₂O. The intense color of the complex indicates both that coordination occurs through the bipyridine units and that it is a low spin species, as confirmed by its unshifted ¹H NMR spectrum. As an unsymmetrical bidentate ligand, L could give rise to two isomers, facial (fac) and meridional (mer), of an octahedral tris complex, and the relatively poor resolution of the ¹H NMR spectrum (compared to that of the ligand) and, in particular, the presence of two NH signals of unequal intensity are consistent with the superposition of three sets of signals for the three symmetry-inequivalent ligands of the *mer* isomer (Figure 6). Other measurements (IR, MS-see Experimental and SI for details, Figures S15-S19) were consistent with the composition as a tris complex.

The complex is of very low solubility in TCE, but an absorption spectrum could be obtained (Figure S23), which

showed a significant temperature dependence. In the better solvent CH₃CN, the changes were much greater (Figure S23) but were not clearly associated with the development of a new absorption band. For an ionic complex, spectral changes with temperature could be due to changes in the degree of ion association, so that the present measurements were considered to be of ambiguous origin. Importantly, however, the spectra were not detectably time-dependent under any given set of conditions and were identical with those of the recrystallized material structurally characterized (see below) as the mer isomer. Hence, isomerization mer-to-fac seemed not to be detectable in solution but in fact must occur to some extent in DMSO at least, since on prolonged (6 months') standing of a DMSO solution, crystals deposited in low yield proved to contain the fac isomer, apparently of the composition $[FeL_3]_2(SiF_6)(BF_4)_2 \cdot 12H_2O-C2$ (see below).

Structure Determinations. $[FeL_3](BF_4)_2 \cdot 9H_2O$ —C1. Crystals of $[FeL_3](BF_4)_2 \cdot 9H_2O$ —C1 suitable for X-ray diffraction measurements were obtained by slow evaporation of an acetonitrile solution. The crystals gave very weak reflections when using copper or molybdenum radiation, and the structure was eventually obtained using synchrotron radiation.



Figure 5. (a) The unique molecule within the crystal lattice, showing thermal ellipsoidal plot and atom numbering. (b) The lattice, viewed down c, showing its herringbone pattern and the layers, which are traversed alternately by NH···N and CH···N interactions. (c) Portion of the double-stranded polymer formed by NH···N bonding.

The complex deposited as dark red, rhombic crystals, space group Fdd2. Crystal and structure refinement data are given in Table S1 (see SI for further details). The structure determination established that indeed the cation present was the *mer* isomer (Figure 7a), with both enantiomers being present in the lattice, as expected given the space group. While the fact that H atoms of the lattice water molecules could not be located complicated a full analysis of interactions within the crystal structure, the Hirshfeld surface (see SI, Figure S26) of



Figure 6. ¹H NMR (600 MHz) spectra at ambient temperature in MeCN- d_3 of (a) ligand L and (b) complex C1 (concentration: 1.5 × 10^{-3} M).

the cation clearly shows it to be involved in NH...N, N...HN, NH…O, NH…F, CH…O, and C…C interactions with its surroundings. Reciprocal NH…N/NH…N interactions involve only one side of amino-pyrimidine units and then only in two of the three bound ligands, but these interactions alone serve to link the cations into undulating one-dimensional H-bond polymer chains in which the cation chirality alternates along the chain (Figure 7b). While they do not extend to both sides of the amino-pyrimidine unit as in the crystal of the free ligand, they are bolstered by bridging CH…F and NH…F interactions (Figure 7c) on the other flank of the unit. The aminopyrimidine unit of the third ligand appears to be involved in Hbonding interactions with three separate water molecules (two accepting an NH proton and one, on the basis of an N…O separation of 2.81 Å, being an H-bond donor to pyrimidine-N), and this ligand projects from the polymer chain in such a way as to be involved in $C \cdots C$ (stacking) interactions with the bipyridine unit of a ligand on an adjacent chain (Figure 7d). This and further interactions of the water molecules and $[BF_4]^-$ anions give the structure its three-dimensional form but what is striking in a view down a (Figure S24) is that there are channels running parallel to a which appear to be largely occupied by water molecules alone. This provided a justification for a more detailed investigation of the thermal stability and porosity of the complex.

Complex $[FeL_3]_2(SiF_6)(BF_4)_2 \cdot 12H_2O$ —C2. The amount of material deposited from the 6-month old DMSO solution of C1, stored under aerial conditions, was too small to permit elemental analyses and spectra to be obtained, so that the composition of this material is based on the structure solution alone. The origin of the $[SiF_6]^{2-}$ anion has not been established, but an obvious possibility is that some hydrolysis of the $[BF_4]^-$ to give HF could have occurred and that this would have led to etching of the glass container. What is certain is that the complex is present in its facial form (Figure 8a,b) and that this results in very different interactions of the pendent amino-pyrimidine substituents compared to those in $[FeL_3](BF_4)_2 \cdot 9H_2O$. Viewed down c, the structure displays a hexagonal array of columns of fac- $[FeL_3]^{2+}$ cations, any given hexagon having only 3-fold symmetry, since the chirality of the cations, constant in a particular column, alternates from one column to the next. Within a column, disordered BF₄⁻ anions separate the cations, being largely included within the cavity formed by the three identically oriented amino-pyrimidine



Figure 7. (a) A thermal ellipsoid plot (ORTEP) representation of the C1 complex. (b) Portion of the undulating one-dimensional polymer chain formed by NH…N/N…HN bonding (shown as dashed lines) between cations, the sequence shown having a $\Lambda\Lambda\Lambda$ alternation of chirality. (c) The complete set of weak interactions (dashed lines) evident on the Hirshfeld surface of the cation (complete for the central cation only). Red circles indicate water-O atoms on which the protons were not located. (d) Two side-by-side adjacent polymer strands showing the partial interpenetration resulting in the stacking interactions shown in c.

substituents on one cation. Each hexagonal array of cation plus BF_4^- columns encloses a channel in which are found SiF_6^{2-} anions and the water molecules, each fluorine on Si being H-bonded to a separate water molecule, the $(SiF_6^{2-})(OH_2)_6$ units thus formed being bridged by an additional six water molecules. While partial occupancy of B and F sites complicates analysis of the cation interactions, the Hirshfeld surface for the cation provides evidence for CH…C, CH…O, CH…F, NH…F, and pyrimidine-N…H(water) interactions only (Figure 8c), with NH…N interactions as seen in both L and $[FeL_3](BF_4)_2.9H_2O$ absent. The average distance measured between Fe and nitrogen atoms (1.96 Å) clearly indicates a lack of oxidation of the central metal ion, which despite the presence of atmospheric oxygen remained at a +2



Figure 8. (a) A thermal ellipsoid plot (ORTEP) representation of the FeL₃ *fac*-complex molecule with both two BF₄ and one SiF₆ counterions showing their mutual orientation in the $[FeL_3]_2(SiF_6)-(BF_4)_2\cdot12H_2O$ crystal lattice. (b) The 3-fold symmetric *fac*- $[FeL_3]^{2+1}$ cation found in the crystal of $[FeL_3]_2(SiF_6)(BF_4)_2\cdot12H_2O$, shown as the Δ enantiomer without (left) and with (right) included BF₄⁻ anions (shown as if all sites are fully occupied). (c) The complete set of interactions of one ligand unit as revealed on the Hirshfeld surface (pale blue = F, light pink = B, green = Si).

oxidation state. Such stabilization of Fe(II) against atmospheric oxidation by the binding of 2,2'-bipyridine and/or related ligands has been previously reported in the literature.¹⁴

Sorption Studies. Metal-organic assemblies, including coordination polymers, exhibit a regularity of the framework, which in most cases provides void space regions of desirable size, shape, and functionality. Crystal structure analysis revealed a significant difference in the porosity between organic and metal-organic polymers, L and C1, respectively. Void space calculations, using a probe radius of 1.2 Å, indicated that a supramolecular polymer based on L contains no apparent void space, while coordination polymer C1 possesses available space of 2462 Å³, which is 12.8% of unit cell volume (SI, Figure S28). Nonetheless, we decided to perform an analysis of gas sorption for both our H-bond organic and metal-organic polymer systems. Important is that only two of the three NH₂ groups in the iron complex are involved in hydrogen bond formation so there is one free amine group that could potentially be able to bind gases, either through Hbonding or nucleophilic attack on an electrophilic center. However, the amino group has a trigonal form, which may

mean that the lone electron pair is involved with the aromatic π system and thus would be ineffective as a nucleophile. In the crystal of the ligand, both H atoms of each amino group are involved in hydrogen bonding, and the N atoms are again trigonal and presumably at best weakly nucleophilic, so that it was anticipated that the solid ligand would have a lesser potential for CO₂ absorption than the complex. Another possibly significant difference between the two materials shown by SEM measurements (Figure 9) was that rapid evaporation of the complex solution provided a seemingly amorphous powder whereas the ligand provided microcrystals.



Figure 9. Scanning electron microscopy (SEM) image on silica surface of (a) iron complex C1 and (b) ligand L.

Thermogravimetric analyses (TGA) of the ligand L (Figure 10a, blue curve) and iron complex C1 (Figure 10a, red curve) were conducted under a flowing nitrogen atmosphere in the temperature range of 25-600 °C. The ligand undergoes partial decomposition just above 150 °C, followed by complete



Figure 10. H-bond organic and metal organic polymers analysis. (a) The thermogravimetric analysis (TG) curve; (b) CO_2 gas sorption isotherms and BET specific surface areas determined by CO_2 adsorption.

decomposition near 300 $^{\circ}$ C, whereas the complex C1, after an initial loss of water below 100 $^{\circ}$ C, remains stable up unto 300 $^{\circ}$ C.

The greater resistance to decomposition shown by the complex is presumably due to the greater lattice energy of the ionic species. The CO_2 sorption isotherms (Figure 10b) for the two materials showed moderate differences, though the samples here were first treated so as to remove any volatiles. The ligand crystals were degassed at 150 °C for 24 h under a pressure of 0.25 mmHg, while the complex crystals were degassed and dehydrated at 200 °C for 24 h under the same pressure. The specific surface area of the samples was determined from low-temperature nitrogen adsorption/desorption measurements. The N₂ isotherms of both polymers at -196 °C show type II behavior (IUPAC classification)¹⁵ without saturation, indicating only surface adsorption of N₂ molecules. The specific surface area (BET) values obtained were 6.3 m² g⁻¹ for the ligand and 10.5 m² g⁻¹ for the complex. A slightly more pronounced difference between both systems is seen in CO₂ sorption, where the complex is 4-fold more effective than the ligand, with a specific surface area for the complex of 44.6 $m^2 g^{-1}$, when for a ligand it is only 12.4 m^2 g^{-1} . This more effective adsorption is associated with some hysteresis in the isotherm, consistent with some inhibition of desorption due to stronger interactions within the structure of the solid.

CONCLUSION

The transfer of ligand L from its free to a coordinated state in cationic Fe(II) complexes clearly has a major influence on its H-bonding behavior and associated properties. The isomeric form of the complexes also gives rise to major differences, although in both the presently described species, the incorporation of water into the structures is a common factor apparently perturbing the tendency of the amino-pyrimidine unit to undergo self-association. The tetrafluoroborate anion is another perturbing influence, an observation which implies other obvious ways of modifying the solid state structure. An inversion of possible roles of the crystalline solids as gas adsorbents is seen in that, while in the free ligand L the pyrimidine-N sites are blocked as nucleophiles by H-bonding (and the amino-N is trigonal, indicating a low capacity to act as a nucleophile), at least one pyridine-N remains available as a potential nucleophile, while in both the complexes the pyridine-N sites are both blocked by coordination but each retains, in otherwise rather different arrays, one pyrimidine-N which is seemingly unhindered.

EXPERIMENTAL SECTION

All chemicals and solvents were purchased from commercial sources. NMR spectra were acquired on Bruker Fourier 300 MHz or Bruker Avance IIIHD 600 MHz spectrometers and referenced on solvent residual peaks. Variable temperature NMR spectra were recorded on a Bruker Avance III HD 600 MHz spectrometer equipped with external BCU II temperature controller. ESI-MS spectra were recorded on a Bruker Impact HD Q-TOF spectrometer in positive ion mode. IR spectra were obtained with a Jasco 4000 FTIR spectrophotometer, and peak positions are reported in cm⁻¹. Variable temperature UV– vis spectra were recorded on a Jasco V-750 UV–visible spectrophotometer equipped with a Peltier-type temperature controller. Electronic absorption spectra were collected in the 300–450 nm wavelength range, in Hellma Quartz Suprasil cuvettes, of 1 mm path length. Thermogravimetric analysis (TGA) was performed using a STA6000 (PerkinElmer) instrument between 30 and 600 °C in a N₂

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atmosphere with a flow of 20 mL min⁻¹ and a heating rate of 10 °C min⁻¹. The Brunauer-Emmet-Teller (BET) surface areas were determined by N_2 adsorption at -196 °C, whereas the CO_2 adsorption isotherms were determined at 0 °C using a Micromeritics ASAP 2010 sorptometer. Prior to the measurements of adsorption/ desorption isotherms, the samples were outgassed for 20 h under a pressure of 0.25 mmHg. The DLS spectra were recorded on NanoPlus-3 (Nano Particle Size and Zeta Potential Analyzer from Micromeritics Corp). The morphologies and elemental distribution of the obtained materials were characterized by scanning electron microscopy (SEM, XL 30 ESEMFEG, FEI Company). Diffraction data were collected by ω -scan techniques at room temperature for ligand L on a Rigaku Super Nova four-circle diffractometer with an Atlas CCD detector and mirror-monochromated Cu K α radiation (λ = 1.54178 Å) and for complex $[FeL_3]_2(SiF_6)(BF_4)_2 \cdot 12H_2O-C2$ at 100 (1) K, on the Rigaku Xcalibur four-circle diffractometer with an Eos CCD detector and graphite-monochromated Mo K α radiation $(\lambda = 0.71069 \text{ Å})$. Data were corrected for Lorentz polarization as well as for absorption effects.¹⁶ Precise unit-cell parameters were determined by a least-squares fit of reflections of the highest intensity, chosen from the whole experiment. Using Olex2,¹⁷ the structures were solved with the olex2.solve¹⁸ structure solution program using charge flipping for complex C2 and with SHELXT-2013¹⁹ for ligand L and refined with the ShelXL¹⁹ refinement package using least squares minimization. Diffraction data for complex $[FeL_3](BF_4)_2 \cdot 9H_2O-C1$ were collected at 100 K and $\lambda = 0.9763$ Å using synchrotron X-ray radiation at the EMBL P13 beamline of the Petra III storage ring, Hamburg.²⁰ The complex C1 deposited as dark red, rhombic crystals, space group Fdd2. Integration, scaling, and merging of the intensity data were carried out in the XDS package.²¹ The unit-cell parameters, Bravais lattice, and symmetry were determined using the XPREP²² package. The structures were solved by using SHELXT.¹⁹ Detailed analysis of the diffraction data indicated that the crystal appeared to be merohedrally twinned by inversion with two domains. and twin fractions were refined to 0.44 and 0.56, respectively. The structures were refined by using SHELXL²³ with anisotropic displacement parameters for all non-hydrogen atoms and TWIN instruction. All hydrogen atoms were included at geometrically predicted coordinates.

Spectroscopic Data. *L.* Yield: 50%. ¹H NMR (300 MHz, DMSO*d*₆): δ [ppm] 8.98 (d, *J* = 1.8 Hz, 1H, H³), 8.73 (s, 1H, H²), 8.69 (d, *J* = 4.1 Hz, 1H, H⁶), 8.41 (m, 2H, H⁵, H⁹), 8.20 (dd, *J* = 2.4, 8.3 Hz, 1H, H⁴), 7.95 (td, *J* = 1.7, 7.7, 15.5 Hz, 1H, H⁸), 7.45 (m, 1H, H⁷), 6.96 (s 1H, H¹). ¹³C NMR (75 MHz, DMSO-*d*₆): δ [ppm] 163.26, 156.21, 154.97, 153.55, 149.34, 145.89, 137.33, 133.43, 131.26, 124.10, 120.40, 120.25, 118.72. IR (FT-ATR): ν 3316, 3151, 1651, 1589 cm⁻¹. HRMS (ESI) *m*/*z* calcd for C₁₄H₁₂N₅: 250.1087. Found: [L + H]⁺ = 250.1089. Elemental analysis calcd (%) for C₁₄H₁₂N₅: C, 67.46; H, 4.45; N, 28.10. Found: C, 66.41; H, 4.86; N, 28.92.

[*FeL*₃](*BF*₄)₂·9*H*₂O—*C*1. Yield: 80%. ¹H NMR (600 MHz, MeCNd₃): δ [ppm] 8.57 (m 6H, H⁵,H⁶), 8.29 (m, 9H, H²,H⁴), 8.16 (m, 3H, H⁷), 7.49 (m, 9H, H³, H⁸, H⁹), 5.82 (d, *J* = 15.6 Hz, 6H, H¹). IR (FT-ATR): ν 3373, 3196, 1620, 1595, 1024 cm⁻¹. HRMS (ESI) *m*/*z* calcd for C₄₂H₃₃FeN₁₅: 401.6191. Found: [3L + Fe]²⁺ = 401.6198. Elemental analysis calcd (%) for [FeL₃](BF₄)₂·9H₂O: C, 44.27; H, 4.51; N, 18.44. Found: C, 45.17; H, 4.11; N, 19.40.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.0c01019.

Synthesis and NMR analysis of compounds 2, 3, 4, L, C1; ESI-MS analysis, IR spectra, dynamic light scattering analysis of L; scanning electron microscopy image of L; temperature coefficient of the NH signal; crystal data and structure refinement for L and C1; VT–UV–vis analysis for C1 extended structure definition for compounds L and C1 (PDF)

Accession Codes

CCDC 1969978–1969979 and 1970242 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/ cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

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