Hydrogen-Bonded Networks through Second-Sphere Coordination

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Abstract: The reaction of 4,7-phenanthroline (**1**) with aqueous transition-metal complexes $[Mn(H_2O)_6][NO_3]_2$, $[Co(H_2O)_6][NO_3]_2$, $[Ni(H_2O)_6][NO_3]_2$, $[Mn(H_2O)_6][ClO_4]_2$, and $[Co(H_2O)_6][ClO_4]_2$ does not produce coordination complexes between these metal cations and the N-donor ligand as expected. Instead, supramolecular hydrogen-bonded networks are formed between the nitrogen donor atoms of 4,7-phenanthroline and the OH groups of coordinated water molecules; $M{-}O{-}H\cdots N$ interactions. This motif of *second-sphere* coordination for **1** can be exploited as a tool for crystal engineering. As a demonstration of the generality of this new interaction as a supramolecular building block, five X-ray crystal structures are reported that utilise this hydrogen bonding scheme; $[Co(H_2O)_4(NO_3)_2]\cdot(\mathbf{1})_2$ (**2a**), $[Co(MeCN)_2(H_2O)_4][ClO_4]_2\cdot(\mathbf{1})_2$ (**2b**), $[Ni(H_2O)_4(NO_3)_2]\cdot(\mathbf{1})_2$ (**3a**), $[Mn(H_2O)_4(NO_3)_2]\cdot(\mathbf{1})_2$ (**4a**), and $[Mn(H_2O)_6][ClO_4]_2\cdot(\mathbf{1})_4\cdot 4\,H_2O$ (**4b**). Each network involves complete saturation of the hydrogen-bond donor sets between the aqua complex and **1** using primarily $M{-}O{-}H\cdots N(\mathbf{1})$ and $M{-}O{-}H\cdots O$(anion), interactions. Thermogravimteric analysis shows these materials to have stablilities similar to coordination polymers involving metal–ligand bonds; this demonstrates that second-sphere hydrogen bonding has potential for the construction of polymeric metal-containing materials.

Keywords: crystal engineering · hydrogen bonds · N ligands · self-assembly · supramolecular chemistry

Introduction

The drive to produce new technologically relevant materials and understand the intricate details of how molecules assemble into such materials (crystal engineering) has resulted in extensive research into the nature of hydrogen-bonded networks.[1] A synthetic strategy that has received little attention is the systematic application of second-sphere coordination[2] to build such hydrogen-bonded systems. This should be of particular interest as a methodology for incorporating and positioning metal sites and, therefore, potential sources of magnetic and electronic phenomena. Although a limited number of studies have been reported which utilize hydrogen-bond donor ligands such as protonated pyridines[3] or amidiniums[4] and anionic metal complexes as hydrogen-bond acceptors the reverse is relatively unexplored in any systematic fashion. In a proof-of-principle investigation, we report herein the utility of 4,7-phenanthroline (**1**) as an exceptional hydrogen-bond acceptor ligand for assembling three-dimensional hydrogen-bonded networks involving *exclusively* second-sphere coordination to simple first-row transition metal aqua ions; Mn^{II}, Co^{II}, and Ni^{II} (see Figure 1).[5]

There are very few, structurally characterized coordination complexes of **1** in the literature and each of these contains **1** bridging two metal centers by *direct*, first-sphere coordination to the metal ions.[6] The rigid 60° angle provided by **1** results in two basic structural types; an equilateral triangular molecular complex[6a,b] or an alternating wave-patterned one-dimensional polymer (see Figure 2).[6c,d] There is *no* literature precedence for the second-sphere coordination of 4,7-phenanthroline. To put things in perspective, there are over 400 X-ray structures in the CCDC database containing the ubiquitous rigid-rod, ligand 4,4′-bipyridine but *none* involves an exclusively hydrogen-bonded network with a d-block element.[7]

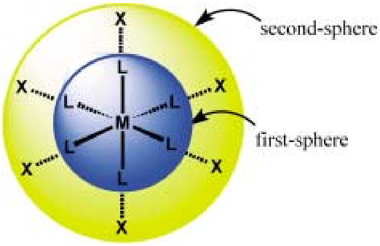

Figure 1. A schematic depiction of the first (blue) and second spheres (yellow) of coordination for an octahedral ML_6 species.

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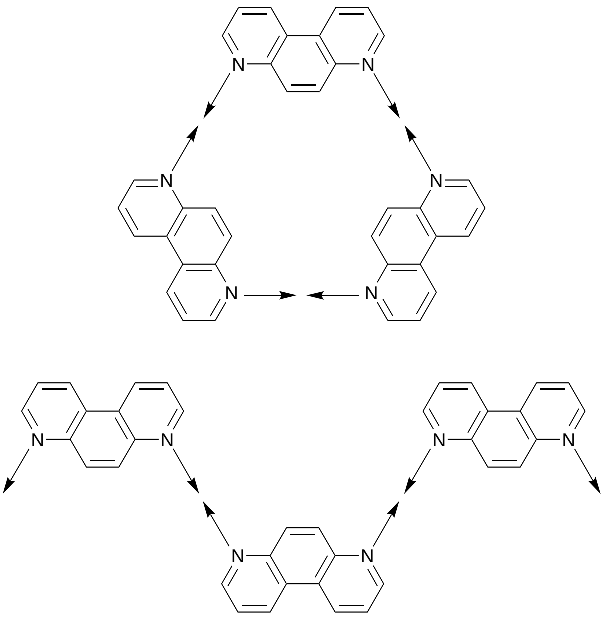

Figure 2. Due to its rigidity and 60° angle **1** can form only two types of metal–ligand structures; a cyclic trimer (top) or a one-dimensional "wave" polymer (bottom). These need not be planar as shown.

Results and Discussion

Mixing one equivalent of an aqua complex $[M(H_2O)_6][X]_2$ ($M = Mn^{II}$, Co^{II}, Ni^{II} and $X = NO_3$, ClO_4) with two equivalents of 4,7-phenanthroline (**1**) in MeCN at room temperature resulted in the formation of X-ray quality crystals for five of the six possibilities: M/X = **2a** (Co/NO_3); **2b** (Co/ClO_4); **3a** (Ni/NO_3); **4a** (Mn/NO_3); **4b** (Mn/ClO_4) (see Tables 1 and 2). None of the compounds contains a 4,7-phenanthroline ligand coordinated directly (M–L) to the metal center. In each case, the N-donor ligand acts as a hydrogen-bond acceptor to metal-bound water ligands yielding a three-dimensional hydrogen-bonded network created by *second-sphere* coordination.

Table 1. Crystal data and details of structure solution and refinement for compounds **2a**, **3a** and **4a**.[a]

	2a	**3a**	**4a**
formula	$C_{24}H_{24}CoN_6O_{10}$	$C_{24}H_{24}NiN_6O_{10}$	$C_{24}H_{24}MnN_6O_{10}$
M_r	615.42	615.20	611.43
crystal system	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$	$P2_1/n$
a [Å]	7.115(2)	7.1057(14)	7.180(2)
b [Å]	14.316(4)	14.245(3)	14.420(5)
c [Å]	12.587(4)	12.599(3)	12.609(4)
β [°]	96.696(6)	96.878(3)	96.184(3)
V [Å^3]	1273.3(7)	1266.1(4)	1297.9(7)
Z	2	2	2
ρ_{calcd} [g cm^{-1}]	1.605	1.614	1.564
$\mu(Mo_{K\alpha})$ [mm^{-1}]	0.745	0.838	0.578
min/max transmission	0.0130/0.0584	0.1132/0.1451	0.0827/0.1451
unique data	5494	5434	5592
R(int)	0.0618	0.0166	0.0394
$R1$ [$I > 2\sigma(I)$]	0.0556	0.0311	0.0498
$wR2$ [$I > 2\sigma(I)$]	0.1435	0.0331	0.0575
$R1$ (all data)	0.0680	0.0828	0.1269
$wR2$ (all data)	0.1518	0.0844	0.1326
data/variables	1817/203	1805/203	1857/203
goodness-of-fit	1.061	1.049	1.008

[a] $T = 298(2)$ K for all data collections.

The nitrate networks **2a** (Co/NO_3), **3a** (Ni/NO_3), and **4a** (Mn/NO_3) form an isomorphous series with simplest formula $[M(H_2O)_4(NO_3)_2] \cdot (\mathbf{1})_2$. Figure 3 (top) shows the two-dimensional array formed by hydrogen bonding between the first-sphere water ligands and the second-sphere 4,7-phenanthroline ligands. Figure 3 (bottom) shows how these two-dimensional networks are further linked through hydrogen bonding into a three-dimensional assembly. Formally, these materials could be considered as co-crystals consisting of two neutral components, $[M(H_2O)_4(NO_3)_2]$ and **1**, in a 1:2 ratio. These molecular units are held together by six hydrogen bonds per formula unit, four O–H···N bonds between coordinated water molecules and **1** and two O–H···O bonds between coordinated water molecules and coordinated nitrate ions. The remaining two O–H groups from coordinated waters are involved in intramolecular chelate-like hydrogen bonds to adjacent nitrate ions. Thus all eight of the hydrogen atoms of the four metal-bound water molecules, all four N atoms from the two molecules of **1**, and all available O atoms of bound nitrate ions are involved in hydrogen bonding. The hydrogen bonding system is totally complimentary and completely saturated.

Figure 4 (top) shows the two-dimensional hydrogen-bonding network formed by the first- and second-sphere coordination spheres of **2b** (Co/ClO_4), which has simplest formula $[Co(MeCN)_2(H_2O)_4][ClO_4]_2 \cdot (\mathbf{1})_2$. Figure 4 (bottom) shows how these arrays are linked together through bridging of metal centers and anions. The difference between **2b** (Co/ClO_4) and **2a** (Co/NO_3) is that two molecules of MeCN now occupy *trans* positions on the metal ion and the non-coordinating perchlorate anions are part of the second sphere

Table 2. Crystal data and details of structure solution and refinement for compounds **2b** and **4b**.[a]

	2b	**4b**
formula	$C_{28}H_{30}Cl_2CoN_6O_{12}$	$C_{48}H_{52}Cl_2MnN_8O_{18}$
M_r	772.41	1154.82
crystal system	monoclinic	triclinic
space group	$P2_1/c$	$P\bar{1}$
a [Å]	8.2998(3)	13.579(5)
b [Å]	13.9644(5)	14.218(5)
c [Å]	15.0389(5)	15.899(6)
α [°]		94.582(7)
β [°]	96.181(1)	114.058(7)
γ [°]		106.126(7)
V [Å^3]	1732.9(1)	2626.6(16)
Z	2	2
ρ_{calcd} [g cm^{-1}]	1.480	1.460
$\mu(Mo_{K\alpha})$ [mm^{-1}]	0.717	0.434
min/max transmission	0.0870/0.1525	0.0941/0.1450
unique data	8362	11504
R(int)	0.0311	0.0385
$R1$ [$I > 2\sigma(I)$]	0.0643	0.0861
$wR2$ [$I > 2\sigma(I)$]	0.0680	0.1006
$R1$ (all data)	0.2003	0.2141
$wR2$ (all data)	0.2148	0.2213
data/variables	3029/240	7391/754
goodness-of-fit	1.022	1.008

[a] $T = 298(2)$ K for all data collections.

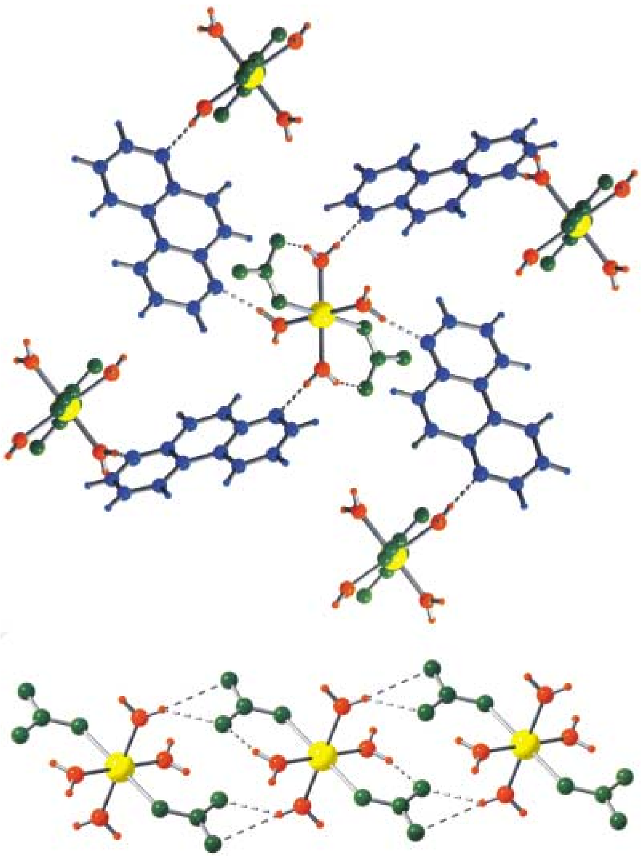

Figure 3. Ball-and-stick representations of the hydrogen-bonding network in **2a**. Top: a two-dimensional network built through second-sphere hydrogen bonding between the first-sphere water ligands and the second-sphere ligands **1** (Co ··· Co 9.9, 13.7 Å). Bottom: the metal centers of these two-dimensional sheets are hydrogen bonded to produce a three-dimensional network (Co ··· Co 7.1 Å); (color key for all figures: yellow = metal, red = first-sphere ligands, purple = lattice water, green = anions, blue = 4,7-phenanthroline, **1**).

of coordination. In **2b**, the metal cations, perchlorate anions, and **1** are held together in a three-dimensional network by eight hydrogen bonds per formula unit, four O–H ··· N bonds between coordinated water molecules and **1** and four O–H ··· O bonds between coordinated waters molecules and non-coordinated perchlorate ions. The coordinated MeCN molecules do not participate in any secondary interactions. As in **2a**, **3a**, and **4a** (M/NO_3) all the hydrogen atoms of the bound water molecules and all the nitrogen atoms from **1** are involved in the hydrogen-bonded network.

Figure 5 (top) shows how the first- and second spheres of coordination for **4b** (Mn/ClO_4), which has simplest formula $[Mn(H_2O)_6][(ClO_4)]_2 \cdot (\mathbf{1})_4 \cdot 4H_2O$, are employed to create a two-dimensional hydrogen bonding array. Figure 5 (bottom) shows how further hydrogen bonding between metal centers and solvent water molecules creates a three-dimensional network comprised of $[Mn(H_2O)_6]^{2+}$ cations, four molecules of solvent water, two non-coordinating perchlorate anions, and four molecules of **1**. This material is knitted together by *twelve* primary hydrogen bonds per formula unit (not counting those involving solvent water), eight O–H ··· N bonds between coordinated water molecules and **1** and four O–H ··· O

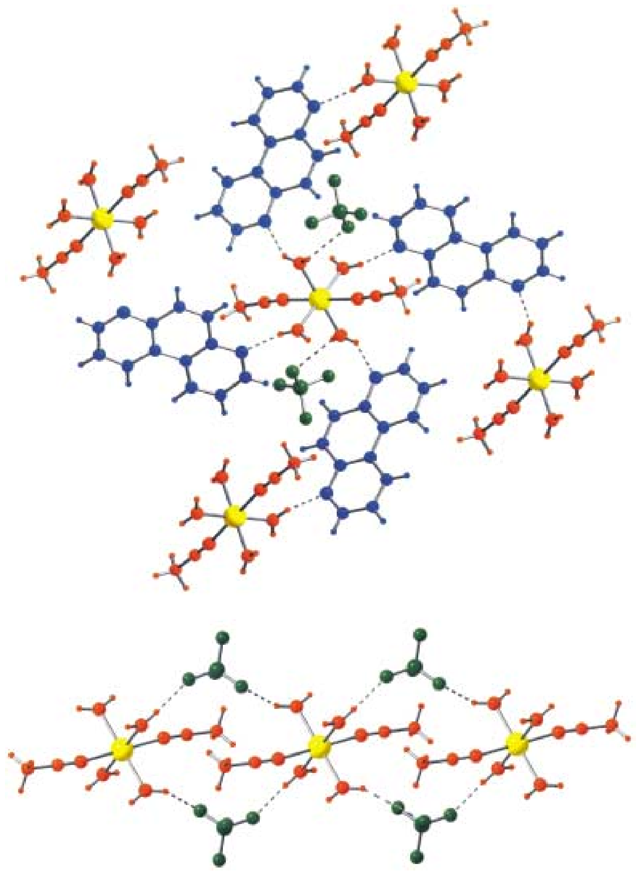

Figure 4. Ball-and-stick representations of the hydrogen-bonding network in **2b**. Top: a two-dimensional network built with second-sphere hydrogen bonding between the first-sphere water ligands and the second-sphere ligands **1** (Co ··· Co 10.3, 12.7 Å). Bottom: the metal centers of these two-dimensional sheets are hydrogen bonded to produce a three-dimensional network (Co ··· Co 8.3 Å); for color scheme see Figure 1.

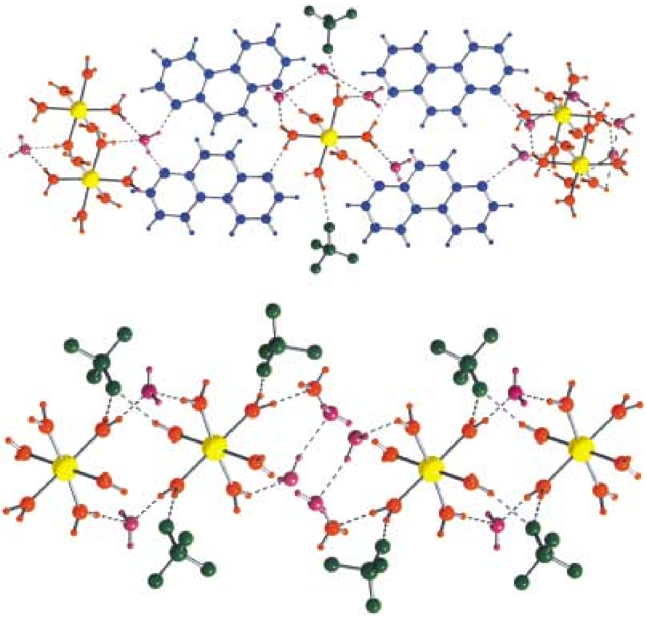

Figure 5. Ball-and-stick representations of the hydrogen-bonding network in **4b**. Top: a two-dimensional network built through second-sphere hydrogen bonding between the first-sphere water ligands and the second-sphere ligands **1** (Mn ··· Mn 13.3, 15.9 Å). Bottom: the metal centers of these two-dimensional sheets are hydrogen bonded to produce a three-dimensioanl network (Mn ··· Mn 8.3 Å); for color scheme see Figure 1.

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bonds between coordinated water molecules and non-coordinated perchlorate ions. Four of the coordinated waters in a square plane are hydrogen bonded to four independent molecules of **1**, which in turn bridge to further $[Mn(H_2O)_6]^{2+}$ ions. The two coordinated water molecules in positions axial to this square plane are hydrogen bonded to the non-coordinated ClO_4^- anions.

All five of the solid-state structures presented herein are held together by a network of second-sphere hydrogen bonds (see Table 3). Although for each metal the first-sphere of coordination is occupied by a slightly different set of ligands, the number of 4,7-phenanthroline ligands involved in formation of the second-sphere coordination network is consistent. In each case, the number of hydrogen-bond donors is matched by an equivalent number of hydrogen-bond acceptors, resulting in saturation of the total hydrogen-bonding complement.

Although these materials contain different arrangements of metal ions, anions, and ligands, the phenomenon of forming purely second-sphere hydrogen-bonded networks results in tightly packed systems with good stability. Thermal gravimetric analyses (TGA) showed coordinated water molecules were lost at typical temperatures (125–140 °C). This is comparable to most coordination compounds; there is no added stability to coordinated ligands as a result of the second-sphere interactions.[8] Lattice water molecules from **4b** are the most easily lost entities (70–100 °C), while coordinated MeCN molecules in **2b** and the molecules of **1** in all compounds were not lost until elevated temperatures (180–200 and 240–270 °C, respectively). Therefore, although these materials are constructed primarily with formally "weak" second-sphere hydrogen bonds, there is nothing inherently unstable about these materials.

Table 3. Hydrogen-bond lengths for **2a**, **2b**, **3a**, **4a**,[a] and **4b**[b].

Interactions	Hydrogen-bond lengths [Å]				
	2a	**2b**	**3a**	**4a**	**4b**
$O(M{-}H_2O)\cdots N(4{,}7{-}phen)$					
O(1)–N(1)	2.74	2.73	2.75	2.75	2.74
O(2)′–N(2)[c]	2.74	2.71	2.74	2.73	2.78
O(3)–N(5)					2.72
O(4)–N(7)					2.81
$O(M{-}H_2O)\cdots O(anion)$					
O(1)–O(4)′[d]	3.16	3.12	3.12	3.19	2.92
O(2)–O(5)[e]	2.71	2.79	2.70	2.74	2.87
O(6)–O(11)					2.97
$N(4{,}7{-}phen)\cdots O(solvent{-}H_2O)$					
N(2)′–O(4W)					2.81
N(4)′–O(2W)					2.78
N(6)′–O(1W)					2.84
N(8)′–O(1W)					2.86
$O(M{-}H_2O)\cdots O(solvent{-}H_2O)$					
O(1)–O(3W)′					2.77
O(2)–O(1W)′					2.77
O(4)–O(2W)					2.76
O(5)–O(4W)					2.70
O(6)–O(1W)					2.76
$O(solvent{-}H_2O)\cdots O(solvent{-}H_2O)$					
O(2W)–O(3W)					2.94
O(3W)–O(4W)					2.84

[a] For **2a**, **3a**, **4a**, **2b**, O(1) and O(2) are bound water molecules and O(4) and O(5) are nitrate or perchlorate O-atoms. [b] For **4a**, O(1)–O(6) are bound water molecules O(7)–O(14) are perchlorate O atoms and O(1W)–O(4W) are solvent molecules. Consecutive pairs of N atoms belong to the same 4,7-phen ligand; N(1) and N(2), N(3) and N(4) etc. [c] O(2)⋯N(3) in **4a**. [d] O(3)⋯O(11)′ in **4a**. [e] O(5)⋯O(7) in **4a**.

Conclusion

This work is relatively preliminary; however, it clearly demonstrates that the concept of second-sphere coordination can be employed successfully as a synthetic strategy for building hydrogen-bonded materials. Each network involves complete saturation of the hydrogen-bond donor sets between the aqua complex and 4,7-phenanthroline by using primarily $M{-}O{-}H\cdots N(\mathbf{1})$ and $M{-}O{-}H\cdots O(anion)$ interactions. These materials have stablilities similar to coordination polymers that involve metal–ligand bonds; this demonstrates that second-sphere hydrogen bonding has potential for the construction of polymeric materials that contain dispersed metal centers and, therefore, potential materials with tailored metal-based properties.

Experimental Section

General methods: All transition metal starting materials, 4,7-phenanthroline and all solvents were purchased from Aldrich Chemicals and used as received. Thermogravimetric analysis were performed on a Netzsch STA449C Instrument under $N_2(g)$ atmosphere at a scan rate of 5 °C min^{-1}.

Materials syntheses: In a typical preparation, two eqivalents of **1** (10.0 mg, 5.55×10^{-2} mmol) and one equivalent of $[Co(H_2O)_6][NO_3]_2$ (5.3 mg, 2.78×10^{-2} mmol) were added to a 10 mL vial and dissolved in MeCN (2 mL). The vial was fitted with a plastic cap into which a glass capillary (~5 cm in length) had been inserted through a small hole. The resulting clear solution was allowed to stand at room temperature while the solvent slowly evaporated. Crystalline material formed within a few days and was isolated by decantation. Yields depended upon the stage at which the crystallization process was interupted; usually when sufficiently sized X-ray quality crystals could be isolated. For one case in which crystal growth was allowed to continue until only the last traces of solvent remained (Co/NO_3), the yield was essentially quantitative.

The Ni/ClO_4 combination produced microcrystalline solid, but not of sufficient quality or size for X-ray diffraction studies. A preliminary X-ray study has shown that if the Ni/NO_3 system is heated to reflux in MeCN, 4,7-phenanthroline will form a Ni–N bond to one end of the ligand, while the other participates in hydrogen bonding. This result will be reported elswhere

Crystallographic studies: Data crystals were mounted on a glass fiber. Reflection data were integrated from frame data obtained from hemisphere scans on a Siemens SMART or Bruker APEX diffractometer with CCD detector. Decay (<1%) was monitored by 50 standard data frames measured at the beginning and end of data collection. Diffraction data and unit-cell parameters were consistent with assigned space groups. Lorentzian polarization corrections and empirical absorption corrections, based on redundant data at varying effective azimuthal angles, were applied to the data sets. The structures were solved by direct methods, completed by subsequent Fourier syntheses and refined with full-matrix least-squares methods against $|F^2|$ data. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms not involved in hydrogen bonding were treated as idealized contributions. All hydrogen atoms involved in hydrogen bonding were refined isotropically. Scattering factors and anomalous dispersion coefficients are contained in the SHELXTL 5.03 program library (Sheldrick, G. M., Madison, WI). CCDC-186387 (**2a**), CCDC-186388 (**3a**), CCDC-186389 (**4a**), CCDC-186390 (**2b**), and CCDC-186391 (**4b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12

Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk).

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[5] Identical reactions were attempted with Fe^{II} starting materials but only the protonated ligand salts H**1**$\cdot$X were isolated. The details of these results will be reported elsewhere.

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[7] A search of the CCDC database gave no hits for structures containing 4,4′-bipy exclusively involved in second-sphere coordination with a d-block transition metal. A small number of complexes were found that contained f-block elements and some were found with both first- and second-sphere or protonated 4,4′-bipy ligands.

[8] For examples of supramolecular encapsulation of aqua metal cations see: S. A. Dalrymple, M. Parvez, G. K. H. Shimizu, *Chem. Commun.* **2002**, 2672 and references therein.

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