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Synthesis, Structure, and Magnetic Properties of $Co_2\{[N(CN)_2]_4bpym\}\cdot H_2O$ and $M\{[N(CN)_2]_2bpym\}\cdot H_2O$ (M = Mn, Fe, Co; bpym = 2,2′-Bipyrimidine)

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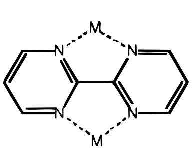
$Co_2\{[N(CN)_2]_4bpym\}\cdot H_2O$ (**1**) and $M\{[N(CN)_2]_2bpym\}\cdot H_2O$ [M = Mn (**2a**), Fe (**2b**), Co (**2c**); bpym = 2,2′-bipyrimidine] have been synthesized and characterized structurally and magnetically. All of the compounds crystallize in the orthorhombic space group *Pnma*. The unit cell parameters for **1** are $a = 16.1684(5)$ Å, $b = 12.9860(3)$ Å, $c = 10.4207(3)$ Å, and $Z = 4$. Compound **1** is a 2-D layered structure with water intercalated between sheets. The sheets are composed of $\cdots M-[NCNCN]_2-M-bpym-M-[NCNCN]_2-M\cdots$ chains, which are linked together by dicyanamides. **2a**−**c** are isomorphic with the unit cell parameters $a = 17.5112(4)$ Å, $b = 11.9955(4)$ Å, $c = 7.4684(2)$ Å for **2a**, $a = 17.5814(7)$ Å, $b = 11.9453(5)$ Å, $c = 7.3292(3)$ Å for **2b**, $a = 17.8642(2)$ Å, $b = 11.9216(2)$ Å, $c = 7.2860(2)$ Å for **2c**, and $Z = 4$ for all. They crystallize as chains containing metal centers coordinated to two bridging dicyanamides, one terminal dicyanamide, one terminal chelating bpym, and one water molecule. **2a**−**c** are the first examples of compounds containing terminal and μ-bound dicyanamides in the same structure. The broad maximum in the magnetic susceptibility of **1** could not be fit to any known dimer models. However, the high-temperature data were fit to the Curie−Weiss expression with $g = 2.86$ and $\theta = -42$ K. **2a**−**c** could best be modeled as uniform 1-D chains with $g = 2.04$, $\theta = -0.76$, and $J/k_B = -0.15$ K for **2a**, $g = 2.34$, $\theta = -7.6$, and $J/k_B = -0.42$ K for **2b**, and $g = 2.58$, $\theta = -5.4$, and $J/k_B = -1.42$ K for **2c**. Because of small exchange coupling throughout the extended networks, no long-range magnetic ordering was observed.

Introduction

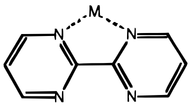
Coordination metal complexes with 2-D and 3-D network structures are currently under intense investigation in the context of molecular-based magnetism.[1] In particular, coordination polymers containing ligands with nitrile moieties have dominated the literature. Since the use of tetracyanoethylene (TCNE) in the synthesis of the first molecular magnet with a magnetic ordering above room temperature, $V(TCNE)_x$,[2] there have been a multitude of polymers created with cyanide,[3] TCNE,[4] 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ),[5] tricyanomethanide,[6] and dicyanamide.[7]

Dicyanamide, which can bind to one,[7a] two,[7b,c] three,[7d] or four[7e] metals, is a versatile building block for multidimensional frameworks. In the case of three-dimensional dicyanamide complexes of $M[N(CN)_2]_2$ (M = V, Cr, Mn, Fe, Co, Ni, Cu) composition, magnetic ordering has been documented at temperatures as high as 47 K (M = Cr).[8] The introduction of ancillary π-conjugated ligands (e.g., pyridine and pyrazine) to these systems has created a wide range of molecular architectures and a greater understanding of the correlation between structure and magnetic behavior.[9]

The bipyrimidine (bpym) ligand is known to facilitate strong antiferromagnetic coupling when coordinating in the bisbidentate mode (**I**) to metals lying in the plane defined by the bpym



I, Bis-bidentate bpym
as found in **1**



II, Bidentate bpym
as found in **2a-c**

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10.1021/ic991244r CCC: $19.00

Table 1. Crystal and Structure Refinement Data for **1** and **2a**−**c**

empirical formula	$C_{16}H_8Co_2N_{16}O$	$C_{12}H_8MnN_{10}O$	$C_{12}H_8FeN_{10}O$	$C_{12}H_8CoN_{10}O$
fw	558.24	363.22	364.13	367.21
space group	*Pnma*	*Pnma*	*Pnma*	*Pnma*
a (Å)	16.1684(5)	17.5112(4)	17.5814(7)	17.8642(2)
b (Å)	12.9860(3)	11.9955(4)	11.9453(5)	11.9216(2)
c (Å)	10.4207(3)	7.4684(2)	7.3292(3)	7.2860(2)
vol (Å^3)	2187.96(11)	1568.77(9)	1539.24(11)	1551.71(4)
Z	4	4	4	4
density (calc) (g cm^{-3})	1.695	1.538	1.571	1.572
μ (mm^{-1})	1.564	0.865	1.003	1.129
temp (K)	173(2)	173(2)	173(2)	298(2)
wavelength (Å)	0.710 73	0.710 73	0.710 73	0.710 73
R [a]	0.0455	0.0794	0.0538	0.0608
R_w [b]	0.1450	0.2027	0.1768	0.1748

[a] $R = \Sigma||F_o| - |F_c||/\Sigma F_o$. [b] $R_w = [\Sigma[w(|F_o|^2 - |F_c|^2)]^2/\Sigma(w|F_o|^2)^2]^{1/2}$ where $w = 1/[\sigma^2(F_o^2) + (0.066P)^2 + 2.6P]$ and $P = (\max(F_o^2,0) + 2F_c^2)/3$.

nitrogens.[10] The two parallel three-atom superexchange pathways provided by bpym are superior to the five-atom pathway of the μ-dicyanamide ligand, and consequently, the magnetic susceptibility of such heteroleptic compounds exhibits a dimer-like broad maximum.[11]

Herein, we present the structural characterization and magnetic properties of several first-row transition metal complexes containing both dicyanamide and bpym ligands. To our knowledge, M{$[N(CN)_2]_2$bpym}·H_2O (M = Mn, Fe, Co) represents the first class of compounds containing multiple dicyanamide coordination modes in the same structure.

Experimental Section[12]

Materials. 2,2′-Bipyrimidine (Lancaster), $MnCl_2 \cdot 4H_2O$ (J. T. Baker), $CoSO_4 \cdot 7H_2O$ (Fisher Scientific), $Fe(BF_4)_2 \cdot 6H_2O$, and $NaN(CN)_2$ (Aldrich) were used as received.

Synthesis. (a) Co_x{$[N(CN)_2]_{2x}$bpym}·H_2O (x = 1, 2) (1 and 2c). A concentrated aqueous solution of $CoSO_4 \cdot 7H_2O$ (208.3 mg, 0.7409 mmol) was slowly added to a concentrated aqueous solution of bpym (58.5 mg, 0.3705 mmol) and $NaN(CN)_2$ (131.9 mg, 1.482 mmol) with continuous stirring. After 3 days of slow evaporation, red crystals with two distinct morphologies were obtained. Small conglomerations of prismatic crystals (**1**) were present with plates (**2c**) in a ∼95:5 ratio. The crystals were filtered, washed with water, air-dried, and separated manually under a microscope. (Found for Co_2{$[N(CN)_2]_4$bpym}·H_2O [$CoC_8N_8H_4O_{0.5}$] (**1**): C, 34.59; H, 1.46; N, 39.60. Anal. Calcd for **1**: C, 34.42; H, 1.43; N, 40.15. Found for Co{$[N(CN)_2]_2$bpym}·H_2O [$CoC_{12}N_{10}H_8O$] (**2c**): C, 39.04; H, 2.17; N, 37.70. Anal. Calcd for **2c**: C, 39.24; H, 2.18; N, 38.15%).

(b) Mn{$[N(CN)_2]_2$bpym}·H_2O (2a). 2a was prepared as described above from $MnCl_2 \cdot 4H_2O$ (134.6 mg, 0.7521 mmol). Crystals suitable for X-ray diffraction were obtained over a period of 3 days. The crystals were harvested, washed with water, and air-dried. (Found for $MnC_{12}N_{10}H_8O$: C, 39.80; H, 2.23; N, 38.43. Anal. Calcd: C, 39.68; H, 2.20; N, 38.57%).

(c) Fe{$[N(CN)_2]_2$bpym}·H_2O (2b). 2b was prepared as described above using $Fe(BF_4)_2 \cdot 6H_2O$ (253.0 mg, 0.7495 mmol) in a Vacuum Atmospheres, Inc. DriLab. After 1 day, crystalline material suitable for single-crystal X-ray diffraction formed. The crystals were filtered, washed with water, and dried under an inert atmosphere. (Found for $FeC_{12}N_{10}H_8O$: C, 38.92; H, 2.04; N, 38.29. Anal. Calcd: C, 39.58; H, 2.20; N, 38.48%).

Table 2. Selected Bond Lengths (Å) and Angles (deg) for the Metal Coordination Spheres of **1** and **2a**−**c**

Co_2{$[N(CN)_2]_4$bpym}·H_2O (**1**)

Co(1)−N(5)	2.075(3)	N(5)Co(1)−N(3)	91.75(13)
Co(1)−N(3)	2.095(3)	N(7)−Co(1)−N(8)	168.70(13)
Co(1)−N(7)	2.103(4)	N(5)−Co(1)−N(2)	173.23(12)
Co(1)−N(8)	2.113(4)	N(3)−Co(1)−N(2)	94.85(12)
Co(1)−N(2)	2.165(3)	N(5)−Co(1)−N(1)	96.44(12)
Co(1)−N(1)	2.167(3)	N(3)−Co(1)−N(1)	171.79(12)
		N(2)−Co(1)−N(1)	76.97(11)

M{$[N(CN)_2]_2$bpym}·H_2O (**2**)

	Mn (**2a**)	Fe (**2b**)	Co (**2c**)
M(1)−N(3)	2.147(5)	2.097(4)	2.092(4)
M(1)−N(5)	2.196(6)	2.125(5)	2.103(5)
M(1)−O(1)	2.192(4)	2.126(4)	2.124(4)
M(1)−N(1)	2.278(3)	2.199(3)	2.151(3)

	Mn (**2a**)	Fe (**2b**)	Co (**2c**)
O(1)−M(1)−N(5)	176.12(17)	175.93(14)	175.75(18)
N(3)−M(1)−N(1)	93.88(19)	94.35(15)	95.45(15)
N(1)−M(1)−N(1)′	71.64(17)	74.97(15)	76.37(17)
N(3)−M(1)−N(3)′	100.4(3)	96.2(3)	92.6(2)

Table 3. Summary of Magnetic Data

	μ_{RT}, μ_B	θ, K	g	J/k_B, K
Co_2{$[N(CN)_2]_4$bpym}·H_2O (**1**)	5.16	−42	2.86	
Mn{$[N(CN)_2]_2$bpym}·H_2O (**2a**)	6.01	−0.76	2.04	−0.15
Fe{$[N(CN)_2]_2$bpym}·H_2O (**2b**)	5.73	−7.6	2.34	−0.42
Co{$[N(CN)_2]_2$bpym}·H_2O (**2c**)	4.96	−5.4	2.58	−1.42

Physical Techniques. Infrared spectra were recorded on a Bio-Rad FTS-40 FTIR spectrometer as KBr pellets in the 4000−400 cm^{-1} region. Magnetic susceptibility measurements were carried out on powdered samples in either gelatin capsules or airtight holders in the temperature range 2−300 K using a Quantum Design MPMS-5XL SQUID ac/dc magnetometer. Samples were cooled in zero field, and data were collected in a 1000 G field upon warming. Diamagnetic corrections for **1** (-169×10^{-6} emu mol^{-1}) and **2a**−**c** ($\sim -265 \times 10^{-6}$ emu mol^{-1}) were calculated from Pascal's constants.

X-ray Data Collection and Structure Refinement. Crystal data collection and refinement parameters are given in Table 1. Suitable crystals for data collection were selected and mounted with epoxy cement on the tip of a fine glass fiber. All data were collected with a Siemens P4 diffractometer equipped with a SMART/CCD detector.

The systematic absences in the diffraction data of all structures are consistent with the orthorhombic space group options *Pna*2$_1$ and *Pnma*. E statistics suggested the centrosymmetric space group, which yielded chemically reasonable and computationally stable results of refinement. Structures **1** and **2a** were solved by direct methods, and compounds

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(12) A compound believed to be Ni_2{$[N(CN)_2]_4$bpym}·H_2O was also synthesized. A structure for the compound could not be obtained because the sample was a powder and elemental analysis was inconclusive. The infrared pattern of the compound is similar to that of compound **1**. (IR, cm^{-1}: 3087 sp, 2315 s, 2259 s, 2189 s, 1627 sp, 1583 s, 1570 sh, 1419 s, 1350 s, 1224 sp, 1036 sp, 752 sp, 683 sp) The magnetic susceptibility exhibits a dimerlike broad maximum, which could not be fit to the Ginsberg and Journaux model for Ni^{II} dimers[18] or a triplet−triplet dimer model.[16.]

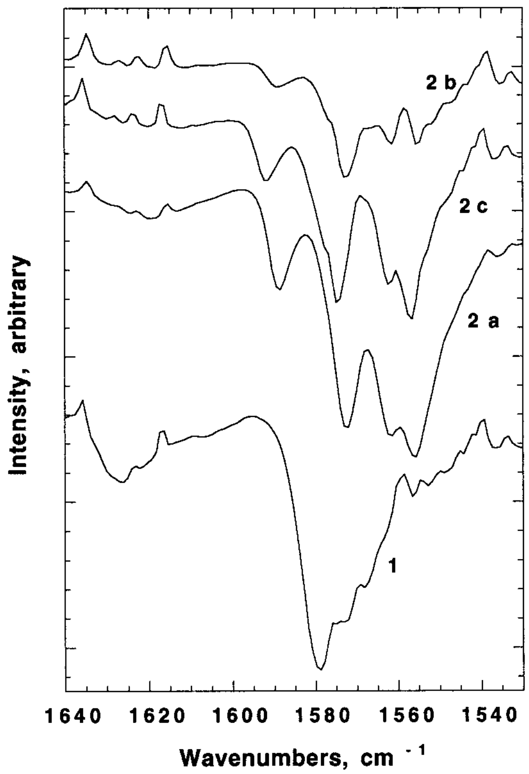

Figure 1. Infrared spectra showing bpym stretching region for **1** and **2a**−**c**.

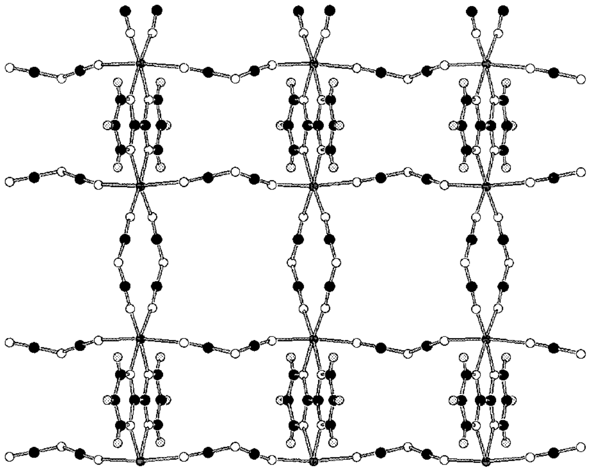

Figure 2. Sheet of $Co_2\{[N(CN)_2]_4bpym\}\cdot H_2O$ (**1**). The second layer is offset 38.2° in the *ab* plane.

2b,**c** were initiated from analogue coordinates. All were completed by subsequent difference Fourier syntheses and refined by full-matrix least-squares procedures. The isomorphous structures, **2a**−**c**, possess crystallographically imposed, mirror plane disorder of the central nitrogen atom in all dicyanamide moieties. All non-hydrogen atoms were refined with anisotropic displacement coefficients, and the hydrogen atoms were treated as idealized contributions. The protons could not be located on either the free water molecule of **1** or the coordinated water molecules of **2a**−**c** and were omitted from the refinement.

All software and sources of the scattering factors are contained in the SHELXTL (version 5.1) program library (G. Sheldrick, Siemens XRD, Madison, WI). Additional structural information including thermal parameters, bond lengths, and bond angles is available as Supporting Information.

Results and Discussion

Infrared Spectra. All compounds displayed strong absorptions in the 2315−2160 cm^{-1} region corresponding to $\nu_{C\equiv N}$ of the dicyanamide ligand. A sharp band at 3087 cm^{-1} apparent in **1** is assigned to hydrogen-bonding interactions, while broad absorptions around 3300 cm^{-1} (ν_s and ν_{as}, OH) were observed for **2a**−**c**. The scissoring motion of unbound water in **1** was observed at 1627 cm^{-1}, while that for bound water was observed near 1590 cm^{-1} in **2a**−**c** (Figure 1). The quasi-symmetric doublet characteristic of chelating bpym appears at 1573 and 1555 cm^{-1} in **2a**−**c**. A smaller peak at 1565 cm^{-1} is also present in these compounds and may be indicative of bis-chelating impurities. **1** shows a strong broad absorption around 1580 cm^{-1} with a shoulder at lower wavenumbers. This pattern has been described as an asymmetric doublet characteristic of ring stretching for bis-chelating bpym.[13]

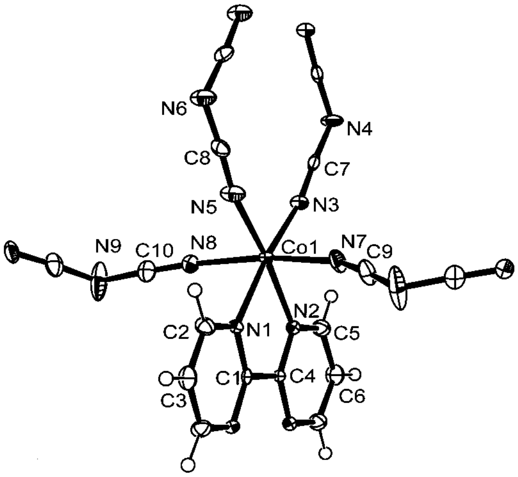

Figure 3. ORTEP diagram (50%) showing the atom labeling scheme of $Co_2\{[N(CN)_2]_4bpym\}\cdot H_2O$ (**1**).

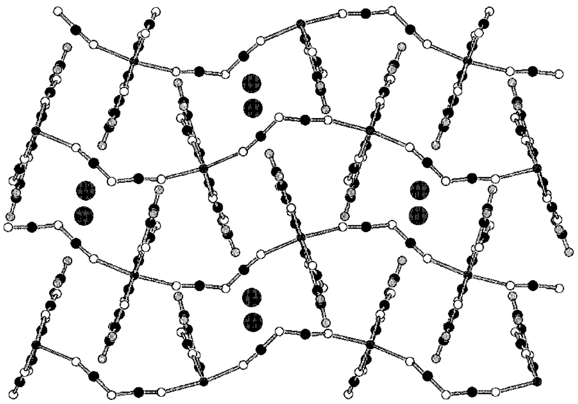

Figure 4. Stacking of $Co_2\{[N(CN)_2]_4bpym\}\cdot H_2O$ (**1**) along the *c* axis. Interstitial water molecules can be seen.

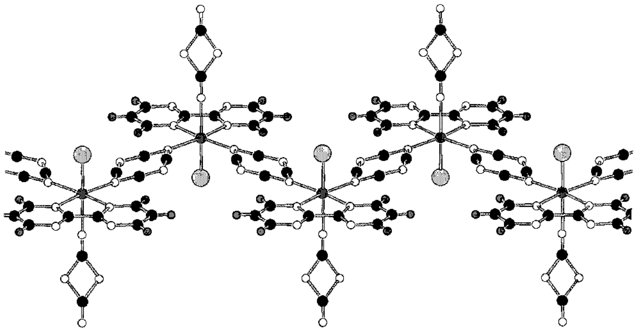

Figure 5. Single chain of **2**.

Description of the Structures. $Co_2\{[N(CN)_2]_4bpym\}\cdot H_2O$ (1). **1** is composed of ···[NCNCN]$_2$−M−bpym−M−[NCNCN]$_2$··· sheets parallel to the *b* axis. These sheets are linked

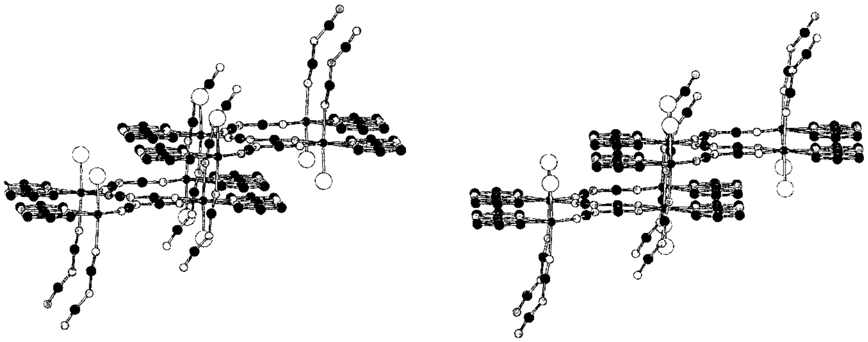

Figure 6. Two chains (bottom left and top right) of **2**. Interdigitation is shown in the central region. Disorder of dicyanamides has been removed for clarity.

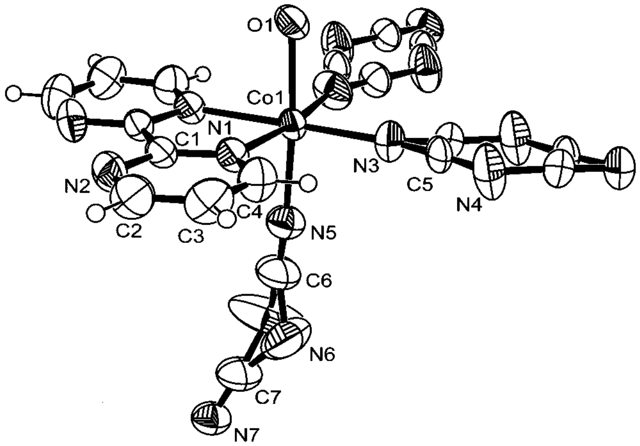

Figure 7. ORTEP diagram (50%) showing the atom labeling scheme of **2**.

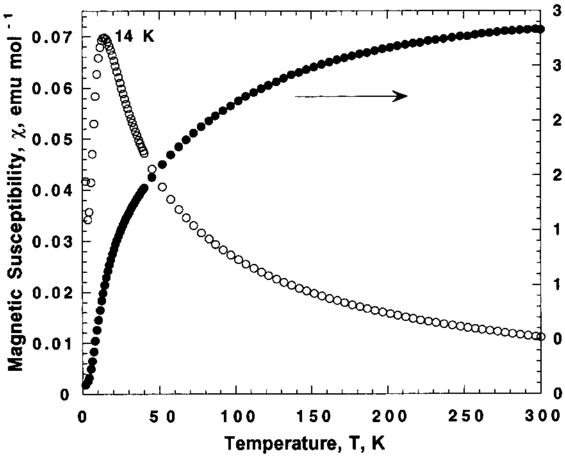

Figure 8. Temperature dependence of χ (○) and χT (●) for **1**.

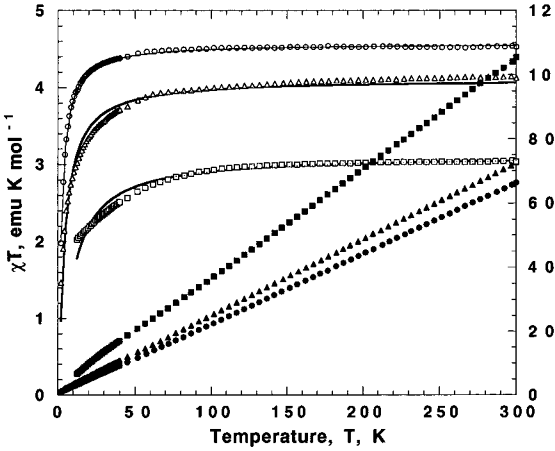

Figure 9. Temperature dependence of χT (○, Mn; △, Fe; □, Co) and χ^{-1} (●, Mn; ▲, Fe; ■, Co). Solid lines represent fits of **2a**−**c** to Fisher 1-D chain models.

via μ-dicyanamide ligands, which propagate along the *a* axis (Figure 2) with adjacent sheets offset by 38.2°. Each Co^{II} is octahedral (Figure 3) with Co···N bonds ranging from 2.075 to 2.167 Å. The Co···Co separation along *b* is 7.220 Å through the μ-dicyanamides and 5.766 Å via the bpym. The μ-dicyanamides coordinating along *a* produce Co···Co separations of 8.288 Å. The N(1)−Co−N(2) bpym bite angle is 76.97(11)°, which leads to the other equatorial angles being slightly larger than 90°. The deviation of the N(7)−Co−N(8) angle from linearity [168.70(13)°] is the result of H-bonding between waters of hydration found between the sheets, which stack along the *c* axis (Figure 4), and amine N's of dicyanamides running along the *a* axis (N···O = 3.050 Å, N···O···N = 91.8°).

M{[N(CN)$_2$]$_2$bpym}·H$_2$O (2). Single-crystal X-ray structures for compounds of this stoichiometry were determined for M = Mn, Fe, Co. These structures are isomorphic and consist of interdigitated 1-D zigzag chains (Figures 5 and 6). These chains are formed by μ-$[N(CN)_2]_2{}^-$-bridged metal centers. One nitrile-bound terminal dicyanamide, one bidentate bipyrimidine (II), and one water molecule occupy the remaining four metal coordination sites (Figure 7). The terminal dicyanamide is rotationally disordered so that the thermal ellipsoids of the carbons could not be sufficiently separated. Therefore, a reliable determination of the N−C−N angles cannot be made. The nearest intrachain M···M distances are 8.983 Å (Mn), 8.630 Å (Fe), and 8.649 Å (Co). Because of the interdigitation of the chains, the nearest interchain M···M distances, 6.723 Å (Mn), 6.722 Å (Fe), and 6.735 Å (Co), are closer than the intrachain distances. As expected, the bpym bite angles, 71.64(17)° (Mn), 74.97(15)° (Fe), and 76.37(17)° (Co), are inversely related to the ionic radii of the metal centers.

Magnetic Properties. The molar magnetic susceptibility, χ, of **1** and **2** were determined between 2 and 300 K (Figures 8 and 9). For **1**, $\chi(T)$ increases with decreasing temperature until a maximum at ~14 K is reached. The broad maximum in $\chi(T)$ implies antiferromagnetic interactions between paramagnetic centers. The antiferromagnetic coupling was confirmed by fitting the high-temperature $1/\chi(T)$ data to the Curie−Weiss expression, $\chi \propto (T - \theta)^{-1}$, with $\theta = -42$ K and $g = 2.86$. The $\chi T(T)$ data decreases steadily upon cooling from 300 down to 2 K. The value of χT at room temperature is 3.33 emu K mol^{-1} (μ_{eff} =

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(13) (a) Berezovsky, F.; Hajem, A. A.; Triki, S.; Pala, J. S.; Molinie, P. *Inorg. Chim. Acta* **1999**, *284*, 8. (b) DeMunno, G.; Julve, M.; Lloret, F.; Faus, J.; Caneschi, A. *J. Chem. Soc., Dalton Trans.* **1994**, 1175.

5.16 μ_B), which is larger than the 1.875 emu K mol^{-1} (3.87 μ_B) expected for isolated $S = {}^3/_2$ ions. This larger value is the result of contributions to the susceptibility from orbital angular momentum at high temperatures, which produces effective moments in the range 4.7−5.2 μ_B.[14]

Numerous attempts were made to model the data for **1** with varying degrees of success. Since it is known that the bpym bridge ($-J/k_B = 0.9-14$ K)[15] is a much better mediator of exchange than μ-dicyanamide ($-J/k_B \approx 0.10-0.18$ K),[9a] we fit the data to a singlet-septet ($S_{tot} = {}^3/_2 \pm {}^3/_2$) dimer model,[16]

$$\chi = C\frac{2\,e^{2x} + 10\,e^{6x} + 28\,e^{12x}}{1 + 3\,e^{2x} + 5\,e^{6x} + 7\,e^{12x}} \tag{1}$$

where $C = Ng^2\mu_B^2/(k_BT)$, N = Avogadro's number, g = Landé value, μ_B = Bohr magneton, k_B = Boltzmann's constant, $x = J/(k_BT)$, and J = exchange coupling constant. This model, however, does not account for spin−orbit coupling and assumes that the dimerlike moieties are magnetically isolated, which they are not. Attempts to utilize a molecular field correction term to quantify the strength of residual interactions through the dicyanamide ligands did not improve the fit. Additionally, we tried the model that accounts for spin−orbit coupling and ligand field distortions developed by Figgis for $^4T_{1g}$ ions.[17] This model was poor because it is meant for isolated monomers and does not include an exchange coupling parameter. Hence, without specific magnetic models describing heteroleptic planar structures we and others[11,18] have been unable to provide detailed analyses of such compounds.

2a−**c** have room temperature χT values of 4.52 (6.01) (M = Mn), 4.11 (5.73) (M = Fe), and 3.07 emu K mol^{-1} (4.96 μ_B) (M = Co). The close approximation between the experimental moment of **2a** and the theoretical spin-only value for $S = {}^5/_2$ ($\mu_{eff} = 5.92$ μ_B) suggests that this compound contains largely isolated spins. However, as is typically observed for Fe^{II} and Co^{II},[19] the room-temperature moments of **2b** and **2c** exceed the spin-only expectation values because of the contribution of orbital angular momentum. For example, the room-temperature moment of **2b** (5.73 μ_B) is significantly larger than the expected spin-only value (4.90 μ_B) for $S = 2$ but is in good agreement with the moment reported (5.68 μ_B) for the related compound $[Fe_3(C_2O_4)_3(4,4'\text{-bpy})_4]$.[20] Above 150 K, the data can be fit to the Curie−Weiss expression giving $\theta = -0.76$ (**2a**), −7.6 (**2b**), and −5.4 K (**2c**), indicating very weak antiferromagnetic coupling.

Because of the 1-D structure for **2**, the magnetic data were fit to a Fisher chain model,[19] which is valid for large values of S (Figure 9),

$$\chi = \frac{Ng^2\mu_B^{\,2}S(S+1)}{3k_BT}\,\frac{1+u}{1-u}$$

$$u = \coth\frac{JS(S+1)}{k_BT} - \frac{k_BT}{JS(S+1)} \tag{2}$$

with $g = 2.04$ and $J/k_B = -0.15$ K for **2a**, $g = 2.34$ and $J/k_B = -0.42$ K for **2b**, and $g = 2.58$ and $J/k_B = -1.42$ K for **2c**. The small values of J/k_B are consistent with weak antiferromagnetic coupling between paramagnetic spin sites. These data, together with the results from the previously reported $Mn[N(CN)_2]_2L_x$ (L = pyridine, 2,2′-bipyridine) compounds,[9] suggest that μ-$[N(CN)_2]_2^-$ coordination provides only weak superexchange interactions as a result of negligible conjugation through the amine nitrogen.

Conclusion

Several heteroleptic compounds were synthesized and characterized utilizing both 2,2′-bipyrimidine and dicyanamide ligands. In addition to containing a unique structural feature, namely, multiple binding modes for dicyanamide, the compounds provided the opportunity to study the effect of bpym chelation on magnetic properties. The superexchange pathway through bpym led to dimerlike behavior in the magnetic susceptibility data of the bisbidentate system. However, in the chain structure, when the bpym superexchange pathway was inoperable, only minimal spin interactions were observed.

Heteroleptic systems give the chemist the opportunity to use multiple building blocks in the design of new materials. The properties of these materials that arise from ligand diversity are an important area of materials science. However, much of the future magnetic research will depend on new heteroleptic-specific models that allow chemists to quantify the amount of metal−metal communication present in these systems.

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Supporting Information Available: Tables listing detailed crystallographic files, atom positional parameters, and bond lengths and angles for $Co_2\{[N(CN)_2]_4bpym\}\cdot H_2O$ and $M\{[N(CN)_2]_2bpym\}\cdot H_2O$ (M = Mn, Fe, Co) (22 pages). This material is available free of charge via the Internet at http://pubs.acs.org.

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