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Structures of $[M(cbim)_4(NO_3)_2]$ [M = Cd(II), Co(II) and Ni(II); cbim = 4′-Cyanobenzyl-1-imidazole] in the Solid State and in Solution

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Mononuclear complexes, $[M(cbim)_4(NO_3)_2]$ [M = Cd(II) (**1**), Co(II) (**2**) and Ni(II) (**3**); cbim = 4′-cyanobenzyl-1-imidazole], were synthesized and their structures were determined by X-ray crystallography. Each metal atom is coordinated by four N atoms of imidazole from four cbim ligands and two O atoms of two nitrate anions with distorted octahedral coordination geometry. All three complexes crystallize in triclinic with space group $P\bar{1}$. There are C–H- - -O, C–H- - -N hydrogen bonds and π-π interactions in the crystal packing of complexes **1**, **2**, and **3**. The compounds were also characterized by ^1H and ^{113}Cd NMR spectroscopy. Highly isotropic shifted signals were observed in the ^1H NMR spectra of complexes **2** and **3** due to the paramagnetic property of the high-spin Co(II) and Ni(II) cores.

In the past decades, numerous metal-directed supramolecular complexes have been obtained by assemblying rationally designed organic ligands with suitable metal ions.[1] The process of such assembly can be described as the result of reading molecular information stored in the ligands by metal ions following the coordination algorithm, such as tetrahedral and octahedral.[2] The structure of a complex is determined by the nature and arrangement of the binding units (ligand) and the coordination geometric need of the metal ions, which determine the steric program and the reading algorithm of the assembly process. Previous studies have shown that both cyano (-CN) and imidazole are functional groups for coordination to transition-metal ions to form metallocomplexes.[3—8] For example, it has been reported that 1,3,5-tricyanobenzene and 1,3,5-tris(4-ethynylbenzonitrile)benzene react with silver(I) trifluoromethanesulfonate to generate two-dimensional (2D) honeycomb and hingelike coordination networks, respectively.[3] 3-Cyano-6-methyl-2(1*H*)-pyridinone (Hcmp), which has both a coordination group of CN and a hydrogen bonding site of NH, reacts with copper(I) salt to form three-dimensional (3D) complexes with a channel framework through the coordination of a cyano group to copper(I) and N–H- - -O hydrogen bonds.[4] On the other hand, the imidazole is a much more common coordination group, not only in synthesized organic ligands, but also in biological systems, e.g. metalloproteins and metalloenzymes, as a sidechain of the histidine residue. *N*,*N*′-(1,4-Butanediyl)bisimidazole formed an interpenetrating 3D network by a reaction with manganese(II) tetrafluoroborate.[5] 1,4-Bis(imidazol-1-ylmethyl)benzene gave an infinite polyrotaxane network by reactions with silver nitrate[6] and zinc nitrate hexahydrate,[7] and an infinite 1D chain with manganese(II) nitrite.[8]

We have recently been exploring the construction of supramolecular complexes with imidazole-containing ligands.[9,10] It has been found that a five-component molecular cage with a tetrahedral zinc ion, $Zn_3(tib)_2(OAc)_6$ [tib = 1,3,5-tris(imidazol-1-ylmethyl)benzene; OAc = acetate anion], was obtained by the self-assembly of a tripodal tib ligand with zinc acetate.[9] However, the reaction of 1,3,5-tris(imidazol-1-ylmethyl)-2,4,6-trimethylbenzene with copper(II) acetate produces an infinite 2D network.[9] A poly-metallocage with a 1D chain-like structure was obtained by the reaction of 4,4′-bis(imidazol-1-ylmethyl)biphenyl ligand with Mn(II) salt.[10]

In order to further investigate the influence of appending a group of 1,4-disubstituted benzene ligand on the formation of supramolecular complexes, 4′-cyanobenzyl-1-imidazole-(cbim) was employed as a ligand. In this ligand, one imidazole group connects to the benzene ring through a methylene group, which is same as that in 1,4-bis(imidazol-1-ylmethyl)benzene; however, another imidazol-1-ylmethyl group at the 4-position of 1,4-bis(imidazol-1-ylmethyl)benzene was replaced by a cyano group in the cbim ligand. Hence, the cbim is an asymmetric ligand. Furthermore, up to now no complexes with a ligand having both cyano and imidazole groups have been reported. It would be interesting to find ligands containing imidazole and cyano groups and their coordination complexes with transition metal ions. In this paper, we describe cadmium(II), cobalt(II) and nickel(II) complexes with the cbim ligand.

Experimental

General Procedures and Measurements. The ligand cbim was prepared acoording to a literature method.[11] Other reagents were commercially available and used as received without further purification. C, H and N analyses were performed on a Perkin-Elmer 240C elemental analyzer, at the Center of Materials Analysis, Nanjing University. 500 MHz ^{1}H NMR spectroscopic measurements were carried out on a Bruker AM-500 NMR spectrometer, using TMS ($SiMe_4$) as an internal reference. 110.9 MHz ^{113}Cd NMR spectrum was recorded on the same NMR spectrometer with a broad-band probe by using a 10-mm (outer diameter) sample tube. The concentrations of the sample were ca. 20 mM and the recycle delay was 8 s (M = mol dm^{-3}). The signal, due to an aqueous solution of $Cd(ClO_4)_2$ (0.1 M) at 298 K, was defined as 0 ppm and used as an external reference in the ^{113}Cd NMR.

Preparation of $[Cd(cbim)_4(NO_3)_2]$ (1). An aqueous solution (5 ml) of $Cd(NO_3)_2 \cdot 4H_2O$ (15.4 mg, 0.05 mmol) was added to an ethanol solution (10 ml) of cbim (18.3 mg, 0.1 mmol) with stirring at 50 °C for half an hour. Single crystals suitable for X-ray diffraction were obtained by slow diffusion of diethyl ether into the clear filtrate for several days. Yield: 75%. Found: C, 54.37; H, 3.93; N, 20.05%. Calcd. for $C_{44}H_{36}N_{14}CdO_6$: C, 54.52; H, 3.74; N, 20.23%. ^{1}H NMR (CD_3CN, 298 K): δ = 7.80 (s, 4H); 7.71 (d, 8H); 7.33 (d, 8H); 7.12 (s, 4H); 7.02 (s, 4H); 5.28 (s, 8H).

Preparation of $[Co(cbim)_4(NO_3)_2]$ (2). The complex was obtained by a reaction of the cbim ligand with $Co(NO_3)_2 \cdot 6H_2O$ following the procedures for complex **1**, as described above. Yield: 80%. Found: C, 57.72; H, 4.27; N, 21.46%. Calcd. for $C_{44}H_{36}N_{14}CoO_6$: C, 57.71; H, 3.96; N, 21.41%.

Preparation of $[Ni(cbim)_4(NO_3)_2]$ (3). The complex was prepared by a similar method to that described for complexes **1** and **2**. Yield: 78%. Found: C, 57.58; H, 4.11; N, 21.34%. Calcd. for $C_{44}H_{36}N_{14}NiO_6$: C, 57.72; H, 3.96; N, 21.42%.

Crystal Structure Determination. The X-ray diffraction intensities were collected using ω-2θ scan techniques on a Rigaku AFC-5R diffractometer with graphite-monochromated Mo $K\alpha$ radiation (λ = 0.7107 Å) for complex **1**. Calculations were carried out on an SGI workstation with the teXsan software package. An empirical absorption correction based on Ψ scans was applied for **1** with transmission factors of 0.892—1.000. No significant decays in the intensities of three standard reflections were observed throughout the data collection. The structure was solved by a direct method using SHELXS-86[12] and refined by a full-matrix least-square method anisotropically for non-hydrogen atoms. The hydrogen atoms were generated geometrically.

X-ray diffraction measurements for complexes **2** and **3** were performed on a Siemens P4 automatic four-circle diffractometer using graphite-monochromated Mo $K\alpha$ radiation (λ = 0.71073 Å). Intensity data were collected in the variable ω-scan mode. The structures were solved by a direct method using SHELXS-86[12] and refined by a full-matrix least-squares calculation on F^2 with SHELXL-93.[13] All non-hydrogen atoms were refined anisotropically, whereas the hydrogen atoms were generated geometrically. Calculations were performed on a PC-586 computer using the Siemens SHELXTL program package.[14,15]

Details of the crystal parameters, data collection and refinement for complexes **1**, **2** and **3** are listed in Table 1, and selected bond distances and angles are given in Table 2.

Results and Discussion

Description of Crystal Structures. The same space group and the similar cell parameters as listed in Table 1 indicate that complexes **1**, **2** and **3** are isomorphous and isostructural. An ORTEP drawing of complex **1** is exhibited

Table 1. Summary of Crystal Data and Refinement Results for Complexes **1**, **2** and **3**

	1	2	3
Chemical formula	$C_{44}CdH_{36}N_{14}O_6$	$C_{44}CoH_{36}N_{14}O_6$	$C_{44}H_{36}N_{14}NiO_6$
Crystal size/mm	0.50 × 0.50 × 0.20	0.35 × 0.35 × 0.15	0.40 × 0.40 × 0.20
Crystal system	Triclinic	Triclinic	Triclinic
Space group	$P1$	$P1$	$P1$
a/Å	8.161(2)	8.061(2)	8.0457(6)
b/Å	8.845(2)	8.767(2)	8.7546(8)
c/Å	17.024(3)	16.830(4)	16.790(3)
α/°	81.28(2)	81.71(2)	81.779(12)
β/°	86.42(2)	87.62(2)	87.802(10)
γ/°	63.38(1)	63.87(2)	63.762(5)
Volume/Å^3	1086.0(4)	1056.4(4)	1049.4(2)
Z	1	1	1
D_{calcd}/g cm^{-3}	1.482	1.440	1.449
F(000)	494	473	474
μ(M$K\alpha$)/cm^{-1}	5.7	4.74	5.31
Total data	5321	4589	4547
Unique data	5000	3727	3697
Observed data	3378	2452	3262
No. of parameters	295	295	295
R, R_W	0.0372, 0.1141		
R indices [I > 2σ(I)]		R_1 = 0.0558	R_1 = 0.0529
		wR_2 = 0.1435	wR_2 = 0.1464
R indices (all data)		R_1 = 0.1629	R_1 = 0.1054
		wR_2 = 0.1796	wR_2 = 0.1670
GOF	1.089	1.018	1.054

Table 2. Selected Bond Distances (Å) and Angles (°) for Complexes **1**, **2** and **3**[a)]

		1	
Cd(1)–N(12)	2.295(3)	Cd(1)–N(22)	2.324(3)
(Cd–N)av	2.310(3)	Cd(1)–O(51)	2.403(3)
O(51)–Cd(1)–O(51)^{i}	180.0	O(51)–Cd(1)–N(12)	95.0(1)
O(51)–Cd(1)–N(12)^{i}	85.0(1)	O(51)–Cd(1)–N(22)	99.9(1)
O(51)–Cd(1)–N(22)^{i}	80.1(1)	N(12)–Cd(1)–N(12)^{i}	180.0
N(12)–Cd(1)–N(22)	94.02(9)	N(12)–Cd(1)–N(22)^{i}	85.98(9)
N(22)–Cd(1)–N(22)^{i}	180.0		
		2	
Co–N(12)	2.134(3)	Co–N(22)	2.109(3)
(Co–N)av	2.122(3)	Co–O(51)	2.213(3)
O(51)–Co–O(51)^{i}	180.0	O(51)–Co–N(12)	81.41(13)
O(51)–Co–N(12)^{i}	98.59(13)	O(51)–Co–N(22)	92.13(13)
O(51)–Co–N(22)^{i}	87.87(13)	N(12)–Co–N(12)^{i}	180.0
N(12)–Co–N(22)	87.17(12)	N(12)–Co–N(22)^{i}	92.83(12)
N(22)–Co–N(22)^{i}	180.0		
		3	
Ni–N(12)	2.099(2)	Ni–N(22)	2.072(2)
(Ni–N)av	2.086(2	Ni–O(51)	2.180(2)
O(51)–Ni–O(51)^{i}	180.0	O(51)–Ni–N(12)	99.09(8)
O(51)–Ni–N(12)^{i}	80.91(8)	O(51)–Ni–N(22)	87.11(8)
O(51)–Ni–N(22)^{i}	92.89(8)	N(12)–Ni–N(12)^{i}	180.0
N(12)–Ni–N(22)	87.45(7)	N(12)–Ni–N(22)^{i}	92.55(7)
N(22)–Ni–N(22)^{i}	180.0		

a) Symmetry code: (i) −x, −y, −z

in Fig. 1 along with the atom numbering scheme. The X-ray crystal structure of the complexes confirms that only the imidazole group of the cbim ligand coordinates to the Cd(II), Co(II) and Ni(II) atoms, and that the cyano group of the ligand remains free of coordination. Therefore, only mononuclear complexes were obtained. Each metal ion is coordinated by four N atoms of imidazole from four cbim ligands with average bond lengths of Cd–N$_{av}$ = 2.310(3), Co–N$_{av}$ = 2.122(3) and Ni–N$_{av}$ = 2.086(2) Å, respectively (Table 2). The four N atoms of N12, N12A, N22, N22A and the metal atom lie strictly on the same plane. The distances of 2.403(3) (Cd1–O51), 2.213(3)(Co–O51) and 2.180(2) (Ni–O51) Å between the metal atom and one oxygen atom of the nitrate indicate the coordination of nitrate to the metal atom. Two nitrate anions coordinated to one metal ion are in a *trans* arrangement. Thus, the coordination geometry around the Cd(II), Co(II) and Ni(II) ions are all distorted octahedral with the N_4O_2 binding set.

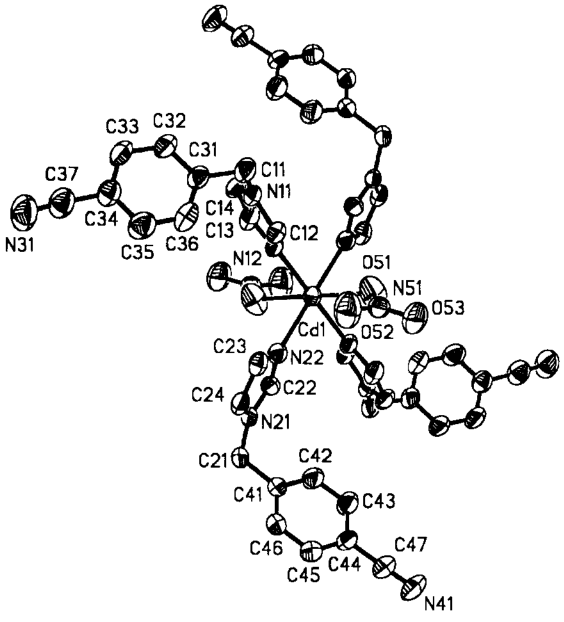

Fig. 1. Molecular structure of complex **1**, thermal ellipsoids are drawn at 50% probability and hydrogen atoms were omitted for clarity.

It is noteworthy that in the reported Cd(II), Co(II) and Ni(II) complexes with imidazole or 1-methylimidazole ligand, the metal ion is coordinated by six N atoms of imidazole without coordination of the nitrate anions.[16,17] For example, it has been reported that $[Cd(1\text{-MeIm})_6](NO_3)_2$ (1-MeIm = 1-methylimidazole) crystallized in monoclinic with the $P2_1/n$ space group and the Cd–N$_{av}$ is 2.360(4) Å.[16] In the Co(II) complex with 2-methylimidazole ligand $[Co(2\text{-MeIm})_4(NO_3)](NO_3)\cdot 0.5CH_3CH_2OH$ (2-MeIm = 2-methylimidazole), one of the nitrate anions coordinated to the Co(II) atom as a bidentate ligand and another nitrate anion did not participate in the coordination.[18] In our complexes **1**, **2** and **3**, however, each metal atom is coordinated by only four cbim ligands with two additional nitrate anions. Such a coordination mode of **1**, **2** and **3** may be caused by hydrogen bonds, π-π interactions and crystal packing, as described below.

A crystal packing diagram of complex **1** is illustrated in Fig. 2 with the hydrogen bonds indicated by dashed lines. There are C–H- - -O and C–H- - -N hydrogen bonds in which the oxygen and nitrogen atoms are from a nitrate and a cyano

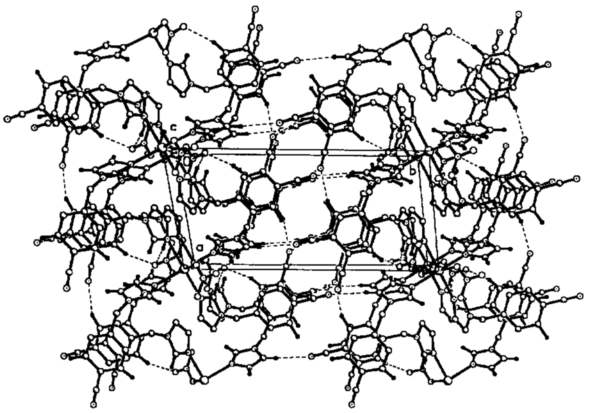

Fig. 2. Crystal packing diagram of complex **1** with hydrogen bonds indicated by dashed lines.

group, respectively. It is notable that cyano N does not participate in the coordination with a metal ion; instead, it forms hydrogen bonds with the benzene ring C–H from the adjacent molecules. The distances and angles for these hydrogen bonds are summarized in Table 3. The crystal packing of complexes **1**, **2** and **3** are also stabilized by π-π interactions. An overlap occurs between the benzene ring planes of two adjacent molecules (Fig. 2). The center-to-center distances between the two nearest benzene ring planes are 4.09 (dihedral angle of 17.9°), 4.04 (dihedral angle of 17.0°) and 4.03 (dihedral angle of 16.9°) Å for **1**, **2** and **3**, respectively. The nearest intermetallic distances of 8.16 (for **1**), 8.06 (for **2**) and 8.05 (for **3**) Å imply the absence of any interactions between two adjacent metal atoms in these complexes. The absence of species with coordination of the cyano group is considered to be caused by a significant difference in the coordination abilities between the imidazole and cyano groups. Such a difference makes the coordination of imidazole to Cd(II), Co(II) or Ni(II) predominantly. In the reported copper(I) complex with dppe and hat-(CN)$_6$ ligands [dppe = 1,2-bis(diphenylphosphanyl)ethane, hat-(CN)$_6$ = hexaazatriphenylene hexacarbonitrile] and manganese(II) complex with 4-cyanopyridine, it was also found that the cyano group does not participate in the coordination.[19]

^{113}Cd, ^{1}H NMR Spectroscopy. ^{113}Cd NMR spectroscopy can be used to investigate the coordination environment of the cadmium(II) ion, since the chemical shift of the ^{113}Cd NMR signal has been proved to reflect the stereochemistry and nature of ligands.[20,21] Complex **1** shows a ^{113}Cd NMR signal at 79 ppm in acetonitrile-d_3 at 298 K. It has been reported that a ^{113}Cd NMR signal at 66 ppm was observed for [Cd(bpy)$_2$(NO$_3$)$_2$] (bpy = α,α'-bipyridine) in DMF.[22] It is believed that the inner-sphere ligands to the cadmium ion are the greatest determinants of ^{113}Cd NMR chemical shifts.[23] Therefore, the observation of the 79 ppm signal for complex **1** suggests that the cadmium(II) ion is also bound with the N$_4$O$_2$ binding set in acetonitrile solution. The previously mentioned [Cd(1-MeIm)$_6$](NO$_3$)$_2$ with CdN$_6$ chromophore exhibited a single ^{113}Cd NMR peak at 177 ppm in methanol solution.[16]

Due to the paramagnetic property of high-spin cobalt(II) and nickel(II) cores, highly isotropic shifted signals were observed in the ^{1}H NMR spectra of complexes **2** and **3** in acetonitrile-d_3 as exhibited in Fig. 3. Three broad peaks of 50, 41, 37 ppm for **2** and 58, 52, 48 ppm for **3**, which appeared at a much lower field side, are reasonably assigned to the imidazole protons due to their proximity to the metal ion. The signals due to the benzene ring and the methylene protons were observed at 11.2, 8.8, 8.3 ppm for **2** and 7.8, 7.3, 6.5 ppm for **3** in acetonitrile-d_3 at 298 K. Similar isotropic

Table 3. Distances (Å) and Angles (°) of Hydrogen Bonding for Complexes **1**, **2** and **3**[a)]

D–H- - -A[b)]	Distance (D- - -A)	D–H–A	Angle (D–H–A)
	1		
C12–H1- - -O52	3.356(5)	C12–H1–O52	137.7
C13–H2- - -O51^{i}	3.253(5)	C13–H2–O51^{i}	118.7
C14–H3- - -N41^{ii}	3.455(5)	C14–H3–N41^{ii}	172.8
C33–H7- - -N31^{iii}	3.420(6)	C33–H7–N31^{iii}	156.5
C35–H8- - -O53^{iv}	3.362(6)	C35–H8–O53^{iv}	152.3
C22–H10- - -O53^{v}	3.388(5)	C22–H10–O53^{v}	158.6
C45–H17- - -N31^{vi}	3.512(6)	C45–H17–N31^{vi}	156.4
	2		
C22–H10- - -O52^{vii}	3.334(6)	C22–H10–O52^{vii}	145.5
C24–H12- - -N31^{vi}	3.472(6)	C24–H12–N31^{vi}	177.9
C43–H16- - -O53^{viii}	3.361(7)	C43–H16–O53^{viii}	148.0
C45–H17- - -N41^{ix}	3.417(8)	C45–H17–N41^{ix}	156.2
	3		
C22–H10- - -O52^{vii}	3.276(4)	C22–H10–O52^{vii}	145.4
C24–H12- - -N31^{vi}	3.482(4)	C24–H12–N31^{vi}	178.4
C43–H16- - -N41^{viii}	3.412(5)	C43–H16–N41^{viii}	155.6
C45–H17- - -O53^{ix}	3.375(4)	C45–H17–O53^{ix}	149.0

a) Symmetry code: (i) −x, −y, −z; (ii) x, −1+y, z; (iii) 2−x, −1−y, 1−z; (iv) 1−x, −y, 1−z; (v) x, y, −1+z; (vi) 2−x, −y, 1−z; (vii) 1−x, −1−y, −z; (viii) 3−x, −2−y, 1−z; (ix) 2−x, −y, −z. b) D: donor; A: acceptor.

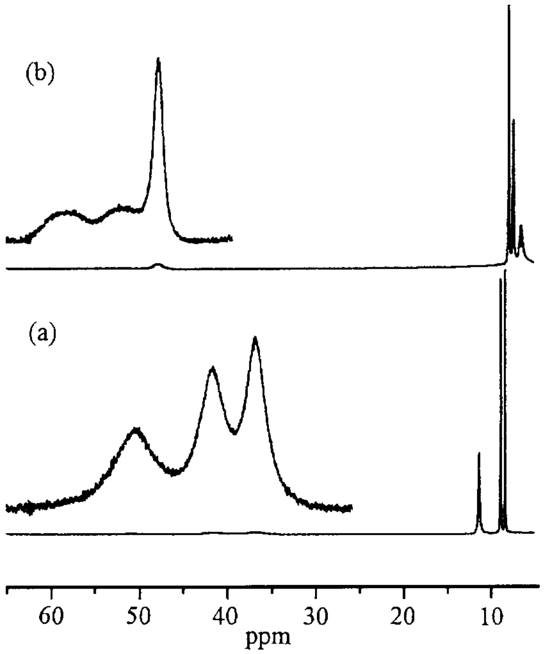

Fig. 3. ^1H NMR spectra of complexes **2** (a) and **3** (b) in acetonitrile-d_3 at 298 K.

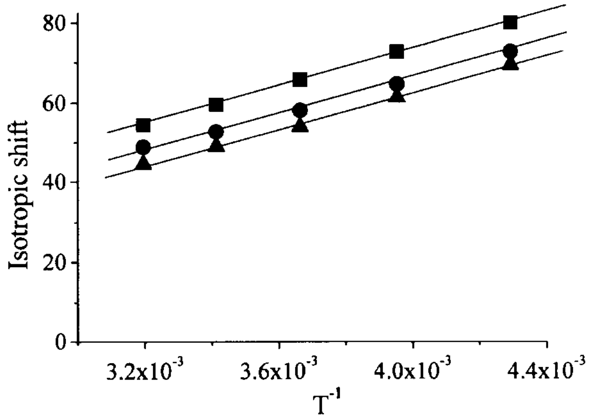

Fig. 4. Temperature dependence of the isotropic shifted signals shown in Fig. 3 (b) vs. T^{-1} for complex **3**. Symbols ■, ● and ▲ refer to the signals at 58, 52 and 48 ppm shown in Fig. 3 (b), respectively.

shifts have been reported for cobalt(II) and nickel(II) complexes with nitrogen-containing ligands.[24,25] The imidazole proton signals were observed at 52, 47 and 32 ppm and the methyl protons appeared at 8 ppm for complex $[Co(1\text{-}MeIm)_6](ClO_4)_2$. A similar ^1H NMR spectrum has been obtained for its Ni(II) analog.[25] The temperature dependence of the isotropic shifted signals was also examined for complexes **2** and **3** in acetonitrile-d_3. All of the signals shift to a lower field with decreasing temperature. A linear correlation between the isotropic shifts and the temperature was obtained for both complexes **2** and **3**; Fig. 4 illustrates the plots for complex **3** as an example. The results suggest that the complexes are not a mixture of aggregated species in solution. ^1H NMR isotropic shifts have been discussed in detail for Co(II) and Ni(II) complexes with the imidazole ligand.[25] It is known that the isotropic shifts of these complexes are primarily contact in nature with only a minor component of a dipolar shift.[24,25] The dipolar contributions due to the magnetic anisotropy in complexes **2** and **3** are considered to be small, since the two nitrate anions coordinated to the metal atoms in the *trans* conformation and the coordination geometry about Co(II) and Ni(II) is octahedral without any serious distortion. Therefore, the observed isotropic shifts of **2** and **3** are predominantly contact.

Conclusion

The present study demonstrated that the formation of a complex is partially controlled by the nature of the organic ligand. In the case of cbim, only the imidazole group coordinated to the metal ion to form mononuclear complexes, although there is another binding site of CN. It is considered that the mononuclear complexes formed by the coordination of imidazole may be too stable to prevent further coordination of the cyano group to the metal ion. Investigations on the reactions between the cbim and metal ions with an effort for the coordination of both the imidazole and the cyano groups to metal ions are now progressing in our lab.

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