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Статья

Investigations into the Coordination Chemistry of 1,3–Bis(2'–benzimidazolylimino)isoindoline

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The N,N,N-tridentate ligand, 1,3-bis(2'-benzimidazolylimino)isoindoline (1) is derived from the reaction of diiminoisoindoline (DII) with 2-aminobenzimidazole and readily binds metal ions. We synthesized several metal complexes of 1 including iron (2), nickel (3), cobalt (4), copper (5) and zinc (6) and were able to structurally characterize all of them as well as free base 1 via single crystal X-ray diffraction methods. Only compounds with a 1:1 metal:ligand stoichiometry were observed, possibly due to the steric bulk of the benzimidazole ligand arms. Ligand 1 binds more tightly than the similar BPI ligand, exhibiting more uniform M-N bond lengths. All compounds exhibit hydrogen bonding via the external N-H group of the benzimidazolyl units, including many cases of extensive hydrogen bond network formation in the solid state.

Keywords: Tridentate ligand, diiminoisoindoline, metal complex, benzimidazole, transition metals, X-ray structure.

Исследование координационной химии 1,3–бис(2'–бензимидазолилимино)изоиндолина

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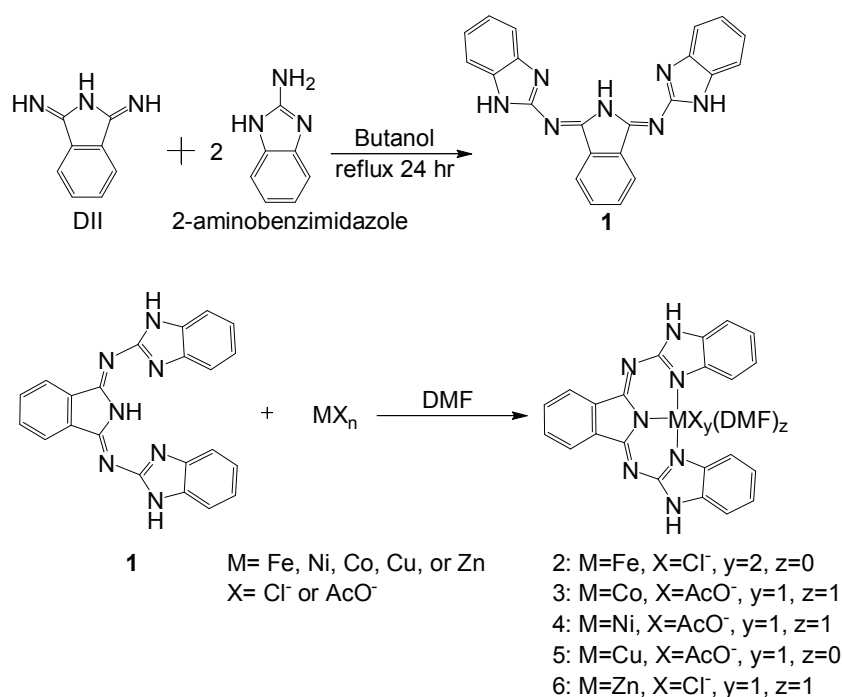*@E-mail: ziegler@uakron.edu*

N,N,N-Тридентатный лиганд, 1,3-бис(2'-бензимидазолилимино)изоиндолин (1), образующийся при взаимодействии дииминоизоиндолина (DII) с 2-аминобензимидазолом, легко связывает ионы металлов. Мы синтезировали и структурно охарактеризовали методом РСА лиганд 1 и его комплексы с железом (2), никелем (3), кобальтом (4), медью (5) и цинком (6). Вследствие наличия объёмных бензимидазольных фрагментов во всех случаях наблюдалось образование комплексов со стехиометрией 1:1. Лиганд 1 образует более прочные комплексы, чем аналогичный лиганд BPI, причём все связи M-N имеют большую выровненность длины. Для всех соединений характерно образование водородных связей внешними N-H группами бензимидазольных фрагментов, что приводит к разветвлённой сети водородных связей в твёрдом состоянии.

Ключевые слова: Тридентантный лиганд, дииминоизоиндолин, металлокомплекс, бензимидазол, переходные металлы, рентгеноструктурный анализ.

Introduction

In the 1950s, Linstead published pioneering work on the synthesis of convenient reagents for the synthesis of the phthalocyanines.[1] The usefulness of phthalocyanines stems from their optical properties leading to their use as bulk dyes in industry and in advanced applications such as photosensitizers in medical applications.[2,3] In particular, Linstead synthesized 1,3-diiminoisoindoline (DII), a key reagent in production of phthalocyanine and the basis of our recent research in the field of phthalocyanine-based precursors and phthalocyanine structural variants.[4-9] DII is a reactive species that can be easily modified through reaction with primary alkyl or aryl amines.[4-13] This property

Coordination Chemistry of 1,3-Bis(2'-benzimidazolylimino)isoindoline

Scheme 1. Synthesis of **1**.

is useful in formation of macrocycles and chelates for further metallation reactions.[14-20] DII can also be used in reactions with subphthalocyanine,[14-20] or for the production of phthalocyanine,[21] and hemiporphyrazines.[22] For the purposes of this report, we'll be focusing on its properties to form a metal chelate similar to bis(iminopyridyl)-iso-indoline.[23,24] Specifically, herein we will present work on the metal binding of 1,3-bis(2'-benzimidazolylimino) isoindoline (**1**, Scheme 1) with elements from the first row of the transition metals.

Compound **1**, has been reported on previously in a number of publications from Speier and co-workers.[25-30] Their synthetic approach differs from the approach presented herein, as they produce **1** directly from phthalonitrile, whereas we isolate the intermediate product of DII prior to reaction with 2-aminobenzimidazole. While Speier and co-workers reported a series of metal complexes of **1**, primarily for the purposes of electrochemical and catalytic studies, most of these compounds were not structurally elucidated via X-ray diffraction methods. The single exceptions are a manganese adduct and a *N*-methylated variant of **1** with copper.[24,26] In this report, we present the first structural elucidation of **1**, as well as a series of first row transition metal adducts of **1**. All of the structures presented here exhibit hydrogen bonding, and in some cases extensive hydrogen bonding resulting in large hydrogen-bonded networks in the solid state.

Experimental

All reagents were purchased from Strem, Acros Organics or Sigma-Aldrich and used as received. Infrared spectra were collected on a Nexus 870 FTIR at the University of Akron. Elemental Analyses were performed by Atlantic Microlab of Norcross, GA 30091 for C, H, and N to demonstrate purity. Mass Spectrometric analyses were carried out at the Mass Spectrometry and Proteomics

Facility at the Ohio State University in Columbus, OH or at the University of Akron in Akron, OH.

X-ray intensity data for the metallated compounds were measured on a Bruker APEX CCD-based X-ray diffractometer system equipped with a Mo-target X-ray tube ($\lambda = 0.71073$ Å) operated at 2000 W power, while the free base, **1**, was collected on an Bruker APEX2 CCD-based diffractometer with dual Cu/Mo ImuS microfocus optics (Cu Kα radiation, $\lambda = 1.54178$ Å). The crystals were mounted on a cryoloop using Paratone oil and placed under a steam of nitrogen at 100 K. The detector was placed at a distance of 5.009 cm from the crystal. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. Absorption corrections were carried out using the SADABS program and the structure was solved and refined using the Bruker SHELXTL Software Package until the final anisotropic full-matrix, least-squares refinement of F^2 converged.

1,3-Bis(2'-benzimidazolylimino)isoindoline (1). The synthesis of **1** has been previously reported using Siegl's procedure.[9] Two equivalents of 2-aminobenzimidazole (1.83 g) was dissolved in a round bottom flask with ~45 mL of butanol. One equivalent diiminoisoindoline (1.0 g) were then added to the round bottom flask. The light green solution turned a light orange upon reaction of the materials. After a 24 hour reflux, the solution was allowed to cool, yielding an orange product that was collected through filtration. Yield: 2.08 g (80 %). X-ray crystallography: crystal data and structure refinement parameters are summarized in Table 1.

FeCl₂(1,3-Bis(2'-benzimidazolylimino)isoindoline) (2). 0.053 mmol of compound **1** (0.079 g), was dissolved in a minimum of DMF. One equivalent of $FeCl_2 \cdot 4H_2O$ (0.042 g) was also dissolved in a minimum of DMF and the two solutions were then combined. The product was isolated by recrystallization using vapor diffusion with the resulting DMF solution and diethyl ether. Yield: 0.046 g (44 %). Calcd for $C_{22}H_{14}N_7Cl_2Fe \cdot 2.55 C_3H_7NO$: C, 51.65; H, 4.66; N, 19.40. Found: C, 51.70; H, 4.72; N, 19.45. ESI MS (positive ion): calcd for $FeH_{14}C_{22}N_7$ ([M-2Cl]⁺) 432.0 found 432.0 M/z. X-ray crystallography: Crystal data and structure refinement parameters are summarized in Table 1.

Co(OAc)(1,3-bis(2'-benzimidazolylimino)isoindoline) (3). The procedure to synthesize **3** was identical to that of **2** using 0.079

Table 1. Single crystal X-ray diffraction parameters for all compounds herein.

Compound	1	2	3	4	5	6
Emp. form	$C_{50}H_{44}N_{16}O_2$	$C_{62}H_{69}Cl_4Fe_2N_{20}O_6$	$C_{27}H_{24}CoN_8O_3$	$C_{54}H_{48}N_{16}Ni_2O_6$	$C_{30}H_{27}CuN_9O_4$	$C_{28}H_{28}ClN_9O_2Zn$
Form. weight	901.01	1443.87	567.47	1134.5	641.15	623.41
Crystal system	Triclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	P-1	P2(1)/n	P2(1)/n	P-1	P2(1)/c	P2(1)/c
a/ Å	7.7287(2)	18.608(12)	8.6790(11)	12.746(2)	11.896(18)	10.001(4)
b/ Å	17.0183(4)	18.168(12)	22.814(3)	13.734(3)	12.751(18)	21.724(8)
c/ Å	17.1125(4)	19.784(13)	12.9592(16)	18.698(4)	19.61(3)	13.687(5)
$\alpha(°)$	84.6490(10)	90	90	70.321(2)	90	90
$\beta(°)$	81.6060(10)	91.977(9)	98.520(2)	72.422(2)	92.960(16)	109.266(5)
$\gamma(°)$	82.2480(10)	90	90	72.583(2)	90	90
Volume (Å³)	2200.11(9)	6684(8)	2537.7(6)	2865.9(9)	2970(8)	2807.1(18)
Z	2	4	4	2	4	4
$D_{calc.}$ (mg/m³)	1.36	1.435	1.485	1.315	1.434	1.475
μ (mm⁻¹)	0.718	0.66	0.723	0.719	0.788	1.014
$F(000)$	4120	2996	1172	1176	1324	1288
reflns collected	22967	43296	21584	22551	24299	22569
indep. reflns	6517	11848	5762	11176	7247	6098
GOF on F²	0.959	1.407	0.997	1.174	0.940	0.870
$R1$ (on Fo², I >2σ(I))	0.0441	0.0559	0.0461	0.0564	0.0491	0.0562
$wR2$ (on Fo², I >2σ(I))	0.1159	0.1158	0.1144	0.0773	0.1295	0.1272
$R1$ (all data)	0.0503	0.0842	0.0580	0.0794	0.0941	0.1137
$wR2$ (all data)	0.1220	0.126	0.1234	0.0824	0.1580	0.164

Note: All datasets were collected at a temperature of 100 K. Absorption corrections were made using multi-scan data colleections and use of the SADABS program during refinement.

g of **1** and 0.052 g of Co(C₂H₃O₂)₂ ·4H₂O. Yield: 0.090 g (76 %). Calcd for C₂₄H₁₇N₇O₂Co·0.5 C₃H₇NO·1.25 H₂O: C, 55.34; H, 4.19; N, 18.98. Found: C, 55.37; H, 4.23; N, 18.91 %. IR bands (cm⁻¹): 1657 w, 1546 s, 1516 s, 1450 m, 1429 m, 1192 m, 1114 m. ESI MS (positive ion): calcd for CoH₁₇C₂₄N₇O₂ (M⁺) 494.08 found 494.06 M/z. X-ray crystallography: Crystal data and structure refinement parameters are summarized in Table 1.

Ni(OAc)(1,3-Bis(2'-benzimidazolylimino)isoindoline) (4). The procedure to synthesize **4** was identical to that of **2** using 0.079 g of **1** and 0.052 g of Ni(C₂H₃O₂)₂·4H₂O. Yield: 0.025 g (21 %). Calcd for C₂₄H₁₇N₇O₂Ni·1C₃H₇NO (DMF solvent molecules) + 0.6 H₂O: C, 56.10; H, 4.39; N, 19.38; O, 9.96. Found: C, 56.46; H, 4.74; N, 18.95; O, 9.80 %. IR bands (cm⁻¹): 1654 w, 1526 s, 1514 s, 1448 m, 1430 m, 1192 m, 1119 s. ESI MS (positive ion): calcd for NiH₁₄C₂₂N₇ ([M-OAc]⁺) 434.00 found 434.06 M/z. X-ray crystallography: Crystal data and structure refinement parameters are summarized in Table 1.

Cu(OAc)(1,3-Bis(2'-benzimidazolylimino)isoindoline) (5). The procedure to synthesize **5** was identical to that of **2** using 0.079 g of **1** and 0.038 g of Cu(C₂H₃O₂)₂. Yield: 0.056 g (54 %). Calcd for C₂₄H₁₇N₇O₂Cu: C, 57.89; H, 3.24; N, 19.69 Found: C, 57.87; H, 3.38; N, 19.77 %. IR bands (cm⁻¹): 1551 s, 1511 s, 1452 m, 1428 m, 1191 m, 1125 m. ESI MS (positive ion): calcd for CuH₁₇C₂₄N₇O₂K ([M+K]⁺) 537.79 found 537.88 M/z. X-ray crystallography: Crystal data and structure refinement parameters are summarized in Table 1.

ZnCl(1,3-Bis(2'-benzimidazolylimino)isoindoline) (6). The procedure to synthesize **6** was identical to that of **2** using 0.079 g of **1** and 0.029 g of ZnCl₂. Yield: 0.082 g (63 %). Anal. Calc. for C₂₂H₁₄N₇ClZn·1C₃H₇NO (DMF solvent molecules) + 1.65 H₂O: C,

51.77; H, 4.22; N, 19.32. Found: C, 52.12; H, 3.94; N, 18.90 %. IR bands (cm⁻¹): 1595 s, 1559 m, 1500 s, 1429 s, 1186 w, 1094 m, 1042 m. ESI MS (positive ion): ZnH₁₄C₂₂N₇ ([M-Cl] ⁺) 440.00 found 440.06 M/z. X-ray crystallography: Crystal data and structure refinement parameters are summarized in Table 1.

Results and Discussion

Speier and co-workers previously synthesized compound **1** directly from phthalonitrile using Siegl-like conditions,[26] however 1,3-diiminoisoindoline (DII) can be conveniently used as an alternate reagent. DII can be readily synthesized via bubbling ammonia gas through a methanol solution of phthalonitrile with sodium metal in nearly quantitative yield,[1] after which the reaction shown in Scheme 1 produces compound **1** resulting in 80 % yield. We observed an overall yield of 76 % which is comparable to the 71 % yield found by Speier and co-workers starting directly from phthalonitrile.[25] Compound **1** was dissolved in DMF for crystal growth via vapor diffusion with diethyl ether. Very long needle-like crystals formed that were suitable for structure elucidation by X-ray diffraction methods (see Figure 1 and Table 1).

Compound **1** has three ionizable protons, one on the isoindoline nitrogen and one on each of the benzimidazole rings. As will be demonstrated below with the metal complexes, often only the isoindoline proton will be
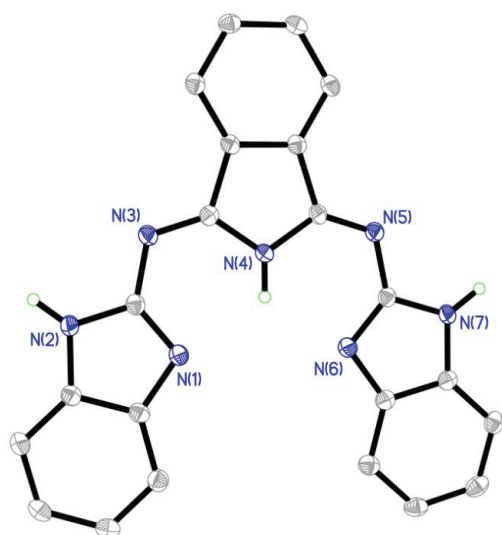
Figure 1. Molecular structure of **1** with non-ionizable hydrogen atoms omitted for clarity and thermal ellipsoids modelled at 35 % occupancy.

removed upon formation of an *N,N,N*-tridentate ligand. As a result, this ligand functions as a monoanionic ligand. Metal adducts formed with dicationic metal species may be capable of forming octahedral metal complexes upon binding of two equivalents of **1**. However, this was not observed in compounds **2-6**. Others have reported formation of 2:1 ligand:metal complexes for compound **1**,[27,28,30,31] however no such structures were observed in our work, and there are no examples of structurally elucidated 2:1 complexes. Compound **1** exhibits hydrogen bonding between the external imidazole N-H groups and solvent DMF molecules. These intermolecular H-bonds have heteroatom distances of ~2.83-2.88 Å. Intramolecular H-bonding forces also likely play a role in the internal structure of the *N,N,N*-core with distances between the isoindoline N-H and the unprotonated imidazole nitrogen atoms of ~2.69-2.72 Å. The compound is planar with a slight twisting of the aminobenzimidazole substituents. The plane as defined by the benzene ring of the

aminobenzimidazole units lie at angles of ~13.2° and ~6.4° (as measured by the Mercury program via the crystallographic cif file) relative to the DII plane, as well as an angle of ~6.9° in relation to one another.

With the crystal structure of the manganese adduct of this ligand having been previously elucidated by Speier and coworkers,[26] we focused on synthesizing complexes with this ligand using the remaining middle and late first row transition metals. Upon mixing of DMF solutions of $FeCl_2 \cdot 4H_2O$ and **1** followed by vapour diffusion crystal growth using diethyl ether, single crystals of **2** formed. The synthesis of this compound was previously reported by Speier *et al.*,[29] however the structural data was not reported. Based on the stoichiometry observed in the solid state, the iron cation is in the +3 state with two chlorides occupying the additional coordination sites giving a trigonal bipyramidal structure. Examination of the bond lengths also supports an assignment of Fe(III). The Fe-N bonds in **2** are relatively short ranging from 2.045(3)–2.073(3) Å, whereas Fe(II)-N bonds would be approximately a tenth of an angstrom longer.[32] The Fe(III)-Cl bonds in **2** are also ~0.1 Å shorter than the Fe(II)-Cl bonds in the referenced structure.[32] We again observed hydrogen bonding of the N_{Im}-H units with the solvate molecules. Upon chelation to the iron atom, the ligand adopts a more rigid planar conformation, with angles of ~2.4° and ~3.9° between the isoindoline plane and that of the aminobenzimidazole units and an angle of ~4.1° between the two aminobenzimidazole rings. All the remaining metal complexes were produced using the same method as for **2**, and with the same vapor diffusion procedure. The synthesis of the cobalt complex, **3**, involved reaction of $Co(C_2H_3O_2)_2 \cdot 4H_2O$ with **1**. A complex of cobalt and **1** was previously reported in the form of the $Co(1)_2$ compound.[27] With the structure of **3** we see our first of two hexacoordinate complexes with a distorted octahedral structure. The cobalt center is formally in the +2 oxidation state, with the ligand and an acetate anion for charge balance. A solvent DMF molecule occupies the sixth and final coordination site. The Co(II)-N bond lengths are similar to other *N,N,N* tridentate ligands, with the central Co-N bond length shorter, 2.0401(19) Å, than the other Co-N bond lengths, 2.0822(19) and 2.1042(19) Å. Again

Table 2. Selected bond lengths of the metal(bimind) complexes, as well as analogous metal(1,3-bis(2-pyridylimino)isoindoline) complexes.

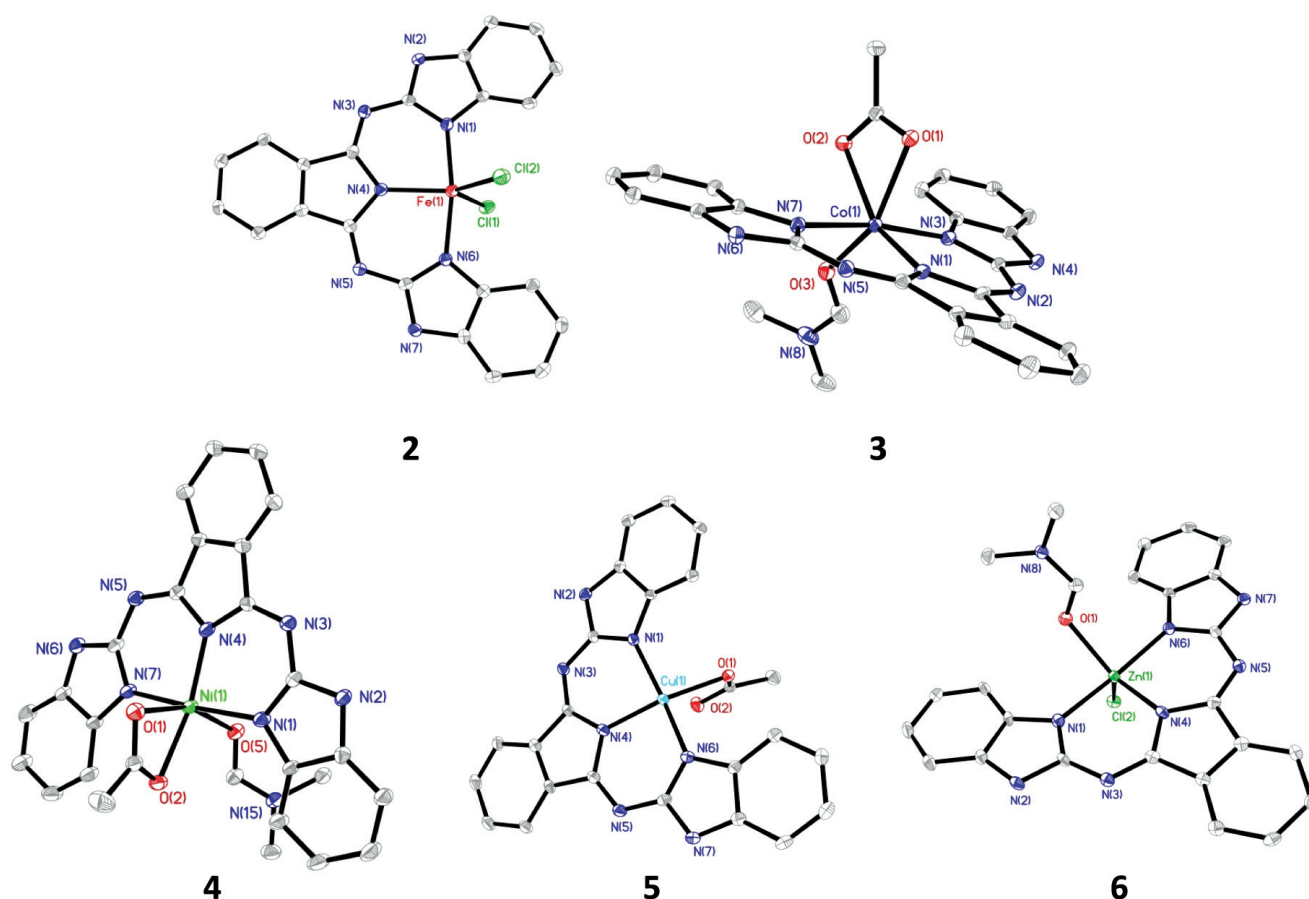| Compound	Isoindoline N-M bond length (Å)	Imidazole/Pyridine N-M bond lengths (Å)
2	2.045(3)	2.064(3), 2.069(3)
Fe(BPI)Cl$_2$[33]	1.963(1)	2.147(1), 2.149(1)
3	2.0401(19)	2.0822(19), 2.1042(19)
Co(BPI)(OCO-Ph)(OO-t-Bu)[34]	1.845(8)	1.95(1), 1.96(1)
4	2.011(3)	2.062(3), 2.076(3)
Ni(BPI)$_2$[35]	2.024(8)	2.155(5), 2.180(5)
5	1.949(4)	1.964(3), 1.970(3)
Cu(BPI)(phenylg lyoxylato)[36]	1.902(3)	2.029(4),2.024(4)
6	2.064(4)	2.081(4), 2.085(4)
Mn(bimind)Cl$_2$[26]	2.007(3)	1.959(2), 1.959(2)
Mn(BPI)Cl$_2$[37]	2.153(4)	2.236(5), 2.262(5)

Figure 2. Molecular structures for all metal complexes **2-6**. Hydrogen atoms omitted for clarity and thermal ellipsoids modeled at 35 % occupancy.

we observe hydrogen bonding involving the N_{Im}-H groups, however in this case the bonding is between neighbouring molecules of the product rather than solvates (see Supporting Information). This complex is less planar than any other the other compounds presented in this report, with angles of ~6.6° and ~11.2° between the isoindoline ring and the aminobenzimidazole rings. The angle between the planes of the two aminobenzimidazole rings is relatively large at ~13.2°.

Reaction of $Ni(C_2H_3O_2)_2 \cdot 4H_2O$ with **1** produced single crystals of **4**. Synthesis of a similar compound with two molecules of **1** bound to Ni was reported previously.[30] The structure is very similar to **3** with the ligand, an acetate anion and a DMF bound to the Ni(II) center in a distorted octahedral geometry. The M-N_{Im} bond lengths are similar to **2** at 2.062(3) and 2.076(3) Å. The M-$N_{isoindoline}$ bond length is significantly shorter than **2**, **3**, or **6** at 2.011(3) Å; with only **5** exhibiting a shorter M-$N_{isoindoline}$ distance. Unlike the other structures, the solvates in this complex were not involved in hydrogen bonding, due to all readily available electron donors and acceptors being involved in intermolecular hydrogen bonding between neighboring metal complexes. Hydrogen bonding between adjacent molecules occurs either through a single H-bond between one of the N_{Im}-H units and the acetate anion, or through two H-bonds between the opposite N_{Im}-H unit and nearby imine. The benzimidazole engaged in multiple hydrogen bonds is more planar in relation to the

isoindoline ring (~2.5°) than the opposite benzimidazole ring (~6.3°).

Compound **5** is produced upon reaction of $Cu(C_2H_3O_2)_2$ with **1**. Similar complexes were reported on by Speier *et al.* involving copper(II) and two ligands of **1**, and a five coordinate Cu complex with one neutral protonated ligand and two monodentate ligands.[28] In the same paper, a structure similar to **5** is presented with a methyl group attached to the exterior imidazole nitrogen and a chloride in place of the acetate. This slightly modified complex of the structures presented here represents the trend we observed, that these complexes exist in the solid state predominately, if not exclusively, in a 1:1 ligand to metal fashion. The geometry of **5** is best described as being highly distorted square planar with a weak interaction at an axial coordination site by the second oxygen atom of the acetate anion at a distance of ~2.51 Å. **5** exhibits the shortest bond lengths of all the compounds present here with 1.964(3) and 1.970(3) Å for the M-N_{Im} bonds, 1.949(4) Å for the M-$N_{isoindoline}$ bond, and 2.009(3) Å for the M-OAc⁻ bond. Significant hydrogen bonding between the N_{Im}-H units is present with either a DMF solvate or acetate of a neighboring **5** molecule. The molecule is relatively planar showing angles of ~3.5° and ~5.1° between the central isoindoline ring and the two benzimidazole rings; as well as a ~6.7° angle between the benzimidazole rings.

Reaction of $ZnCl_2$ with **1** gave rise to **6**. Charge balance for the Zn(II) ion is provided by a single chloride and the

ligand as anions. A DMF from the solvent occupies the fifth and final coordination site, giving the complex a trigonal pyramidal shape. The M-N$_{Im}$ bond lengthes are slightly longer than **2** at 2.081(4) and 2.085(4) Å, the M-N$_{isoindoline}$ bond is the longest of any of the structures at 2.064(4) Å and the M-Cl bond is longer than 2 at 2.3440(14) Å. **6** differs from the other chloride metal complex, **2**, in that the chloride anion is directly involved in the hydrogen bonding network. While the iron complex shows only intermolecular interactions via hydrogen bonding of the N$_{Im}$-H units with the solvent DMF molecules, **6** exhibits both similar N-H bonding to a single solvate as well as a hydrogen bonding interaction of the opposite N$_{Im}$-H to the chloride of an adjacent **6** molecule. The planarity of the molecule is less than most of the metal complexes (with the exception of **3**) with the imidazole rings at angles of ~8.2° and ~7.0° in relation to the isoindoline ring, and at an angle of ~7.3° to each other.

In these compounds, we observe propensity to hydrogen bond either with themselves, solvent molecules, or both. Compounds **1**, **2**, **5**, and **6** all show hydrogen bonding to the solvent DMF molecules. The heteroatom distance of these bonds does not vary a great deal between all of the structures with **2** and **5** having shorter distances of ~2.73-2.74 Å, **6** more intermediate at ~2.84 Å, and the free base **1** having the longest at ~2.83-2.88 Å. **3** and **5** have hydrogen bonding between N$_{Im}$-H and the acetate of a neighboring complex at distances of ~2.73 Å for **3**, and ~2.78 and ~2.86 Å for **5**. **4** is the only example of these compounds for hydrogen bonding involving the *meso*-nitrogen position with distances of ~2.89 and ~2.94 Å. Lastly, **6** shows hydrogen bonding between the coordinated chloride and the N$_{Im}$-H of a neighboring molecule at ~3.19 Å. Figures of the hydrogen bonding networks of these complexes can be found in the Supporting information.

For comparison, one can examine the differences between the chelation of ligand **1** with first-row transition metals to that of the more extensively studied pyridine analog, 1,3-bis(2-pyridylimino)isoindoline, BPI (Table 2). Compound **1** binds with much more symmetric N-M bond lengths, with the N$_{Im}$-M and N$_{isoindoline}$-M bond lengths varying by only ~0.01-0.05 Å. In contrast, the analogous BPI complexes show N$_{isoindoline}$-M bond lengths as much as ~0.2 Å shorter than that of the N$_{py}$-M bond lengths. For Fe(III), Co(II) and Cu(II), the N$_{isoindoline}$-M bond length of **1** is between ~0.05-0.20 Å longer than that of the equivalent BPI compound. This trend reverses itself in regards to the Ni(II) and Mn(III) complexes, which show shorter N$_{isoindoline}$-M bond lengths with **1** than BPI. To our knowledge, to date a similarly structured Zn(BPI) complex has not been structurally elucidated for comparison.

Conclusions

Presented here are the several middle and late transition metal complexes of 1,3-bis(2'-benzimidazolylimino) iso-indoline (**1**) with 1:1 metal to ligand stoichiometries. We were able to elucidate the structures of these compounds along with the free ligand via single crystal X-ray diffraction. Ligand **1** is produced in good yield from a simple synthetic procedure from the starting material DII, and the metal com-

plexes are formed readily simply by mixing DMF solutions of the ligand and metal salts. These data provide important structural insight for DII based ligand systems and build on the synthetic work from Linstead, Speier, and others.[1,25-35] These compounds may have useful applications in formation of new phthalocyanine-like chelates and resultant metal complexes and all of the compounds presented show significant hydrogen bonding in the solid-state. Our group will continue to explore the chemistry of DII in an effort to produce interesting ligand systems and new metal complexes.

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