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Complexes of 1,3-bis(2-thiazolylimino)isoindoline with middle and late first row transition metals

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ABSTRACT

In this communication, we present a study that probes the middle and late first row transition metal chemistry of 1,3-bis(2-thiazolylimino)isoindoline, adding to the known Fe and Cu compounds. Complexes of this ligand with Mn, Co, Zn and a new Fe form are presented and all are structurally characterized by single crystal X-ray methods. The 1,3-bis(2-thiazolylimino)isoindoline ligand can potentially bind via the thiazolyl nitrogen or sulfur atoms; in all of the complexes presented in this report, the N,N,N binding mode is observed exclusively. The ligands bind in a planar configuration, similar to that seen for bis(2-iminopyridyl)isoindoline.

In the 1950s, Linstead and Elvidge presented a series of papers reporting on the chemistry of the diiminoisoindoline (DII) heterocycle [1]. This compound (Scheme 1), which can be considered as a subunit of phthalocyanine, can be readily functionalized. Diiminoisoindoline can be used to generate phthalocyanine analogs known as the hemiporphyrazines [2], as well as chelating ligands [3]. One method for modifying diiminoisoindoline is via reaction with primary alkyl or aryl amines, which results in bis(alkylimino) and bis(arylimino)isoindolines respectively [1]. This reaction has been used to produce tridentate chelates, and was first presented by Linstead and Elvidge in 1952 with the synthesis of bis(2-iminopyridyl)isoindoline (BPI, Scheme 1) [1]. Initial investigations into the metal binding properties of this ligand were presented in the same paper along with its synthesis. Over the decades since its synthesis, the bis(2-iminopyridyl)isoindoline ligand has exhibited rich metal chemistry, binding a variety of transition metal ions [1,3,4]. These complexes have been used to model enzymatic active sites [4,5] and as catalysts for organic transformations [4,6].

The chemistry observed with bis(2-iminopyridyl)isoindoline can readily be extended to other coordinating heterocycles. However, to date, little work has been carried out on chelating bis(arylimino)isoindolines with groups other than pyridine. One metal binding aryl group that has been incorporated into an isoindoline chelate is thiazole. This ring is notable in that there are two potentially coordinating atoms present in the ring: sulfur and nitrogen atoms. The resultant isoindoline adduct is 1,3-bis(2-thiazolylimino)isoindoline (BTI, **1**), which can act as a monoanionic tridentate chelate (Scheme 1). Previously, the chemistry of this ligand with copper has been examined by Meder and Gade [6], Bröring and coworkers have explored the coordination chemistry of this chelate with palladium [4,7], and very recently Pap et al. presented a report on the Fe(III) complex of **1** [8]. Theoretically, compound **1** can bind through NNN, SNN or SNS binding modes; in the iron and copper complexes, the N,N,N mode is observed, but Bröring has reported a SNN mode in the palladium complex of a sterically hindered form of BTI [7]. In this report we present an extension of the coordination chemistry of **1** to additional late and middle first row transition metal ions, including Mn(III), Co(III) and Zn(II) complexes. In addition, we have isolated a variant of the previously reported Fe(III) complex and have elucidated the structure of the free ligand. In all observed cases, the NNN binding mode was adopted by the ligand. The ligand itself binds to the metal ions in a planar configuration with slight deviations of the thiazole rings. Both 2:1 and 1:1 ligand to metal complexes are observed to form with chelate **1**, as seen in the bis(2-iminopyridyl) isoindoline.

The synthesis of **1** has been reported via two pathways: through a modification of the original Linstead and Elvidge procedure in butanol [1], and by the method developed by Siegl using the reaction of phthalonitrile and aminothiazole with $CaCl_2$ as the catalyst (Scheme 2) [4]. We were able to generate compound **1** by use of the former method, which resulted in analytically pure crystals from the reaction solution without any observable phthalocyanine production. These crystals were suitable for X-ray diffraction structure elucidation, and Fig. 1 shows the structure of **1**. Table 1 contains crystal data and elucidation parameters for the structure of **1**. Globally, the structure of **1** resembles that of the bis(2-iminopyridyl)isoindoline chelate. In the free ligand, the nitrogen atoms face the interior of the chelate in a way such that the NNN binding would be preferred. The reason for this orientation is

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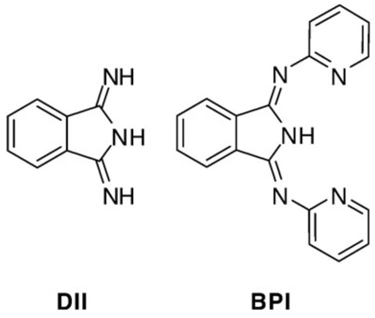


Scheme 1. The structures of DII (left), BPI (center) and compound 1 (right).

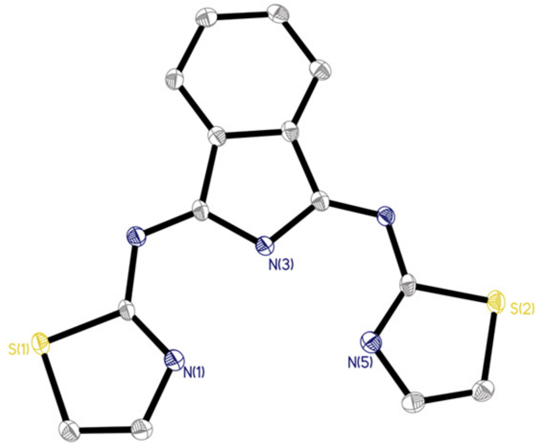


Fig. 1. The structure of **1** with 35% thermal ellipsoids. Hydrogen atoms have been omitted for clarity.

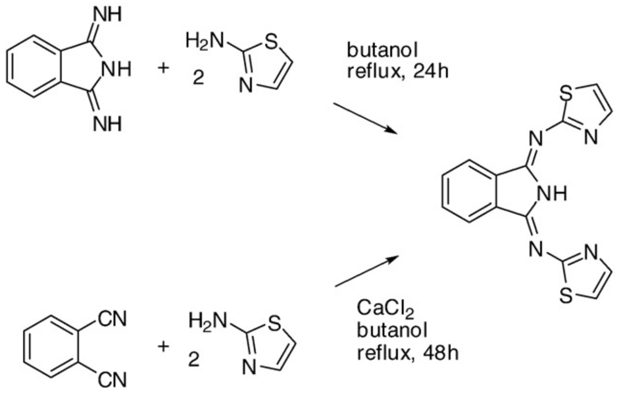
due to hydrogen bonding interactions between the nitrogen atoms on the thiazole ring and the isoindoline NH group; the N–N distances measure ~2.72 and ~2.70 Å. Although in the free base this is the preferred orientation, the thiazole can potentially rotate such that the sulfur would be oriented toward a chelated metal, affording the S-bound coordination isomers. Bröring discusses such coordination isomerism in the palladium complexes of bis(4-tert-butylthiazolyl)indoline, bis(2-iminopicolinyl)isoindolines [7] and bis(2-iminobromopyridinyl)isoindoline [4]. However, as will be shown below, compound **1** was found to chelate to first row transition metals exclusively in the N,N,N binding mode. The preference for this mode most likely results from the hard acid nature of the metals and oxidation states presented in this report, and the weak basicity of the sulfur of the thiazole ring.

We were able to isolate complexes of **1** by reaction of the free base ligand with various metal salts in methanol solution. In all cases, crystalline products formed upon concentration of the reaction solution and, with the exception of the nickel complex, the crystals were suitable for single crystal X-ray structure elucidation. Table 1 contains the X-ray data and elucidation parameters for these structures. Fig. 2 shows the structures of the Mn, Fe, Co, and Zn complexes of **1**. The middle transition metal adducts (**1Mn**, **1Fe** and **1Co**) are all 2:1 ligand to metal complexes, whereas the complex **1Zn** has a 1:1 ligand to metal ratio as seen in the previously elucidated Cu(II) complex. In **1Zn**, the remainder of the coordination sphere is occupied by solvent molecules. Previous work on the bis(2-iminopyridyl)isoindoline ligand has shown that control of reactant stoichiometry can be used to generate 1:1 complexes with metals such as manganese [4].

In all of the metal complexes of **1**, there are several common characteristics observed in the ligand binding geometries. First, the ligand binds in an asymmetric fashion to metals, resulting in different $M-N_{thiazole}$ and $M-N_{indoline}$ lengths. Table 2 lists the M–N bond lengths for the metal complexes presented in this report. As expected, the $M-N_{indoline}$ bonds are appreciably shorter than the $M-N_{thiazole}$ bonds; this primarily results from the negative charge on the isoindoline nitrogen versus the lack of charge on the azole nitrogen. Similar bond length disparities are observed in the bis-pyridine hemiporphyrazines [2] and in bis(2-iminopyridyl)isoindoline complexes, where the $M-N_{isoindoline}$ bonds are markedly shorter than the $M-N_{pyridyl}$ bonds. The bis-ligand complexes **1Mn**, **1Fe** and **1Co** adopt distorted octahedral geometries, with compression along the axis that is aligned with the $M-N_{indoline}$ bonds. As can be seen in Fig. 2, all three homoleptic complexes exhibit nearly identical coordination environments. As mentioned above, the $M-N_{isoindoline}$ are shorter than the $M-N_{pyridine}$ bonds, however in the **1Mn** complex the difference between these bond lengths is much greater than the other two, on the order of <0.25 Å. We can readily determine the oxidation states in these three compounds as Mn(III), Fe(III) and Co(III) respectively by the charges of the ligand (monoanionic) and the presence of an anion in the asymmetric units of **1Mn** and **1Fe**. The anion in the Co(III) complex **1Co** was disordered and difficult to locate on the difference map, and the overall quality of the dataset was limited by twinning problems, but the presence of a normal ^{1}H NMR spectrum along with the observed bond lengths led to an unambiguous Co(III) assignment. Susceptibility measurements as well as bond lengths can also be used to determine the spin states of these three compounds. For the Fe(III) complex, we observed short bond lengths and a susceptibility ($\mu_{eff} = 3.91$ BM) that correlate with an intermediate spin system ($S = 3/2$), whereas in the Mn(III) compound we observed a

Table 1
X-ray data collection and structure parameters for the compounds presented in this report. All structures were collected at 100(2) K.

Compound	**1**	**1Mn**	**1Fe**	**1Co**	**1Zn**
Empirical formula	$C_{12}H_9N_5S_2$	$C_{30}H_{18}C_{l6}N_{11}O_3S_4Mn$	$C_{30}H_{24}N_{11}O_5S_4Fe$	$C_{28}H_{16}N_{10}S_4Co$	$C_{17}H_{20}N_5O_7S_2ZnCl$
Formula weight	311.38	976.43	802.69	679.68	571.36
Crystal system space group	Monoclinic, P2(1)/c	Monoclinic, P2(1)/c	Monoclinic, P2(1)/c	Monoclinic, Pc	Triclinic, P-1
a, Å	14.678(3)	11.5686(15)	12.0797(10)	14.513(4)	9.371(4)
b, Å	4.6240(10)	28.696(4)	15.4733(12)	15.229(5)	10.272(5)
c, Å	20.047(4)	11.2240(15)	17.5335(14)	16.749(5)	12.285(5)
α, °	90	90	90	90	98.442(7)
β, °	102.146(3)	92.523(2)	91.5210(10)	115.431(5)	95.652(7)
γ, °	90	90	90	90	109.691(7)
V, Å [3]	1330.2(5)	3722.4(9)	3276.1(5)	3343.1(18)	1087.3(8)
Z	4	4	4	4	2
D_{calc}, mg m^{-3}	1.555	1.742	1.627	1.35	1.745
Unique reflections	10054	30923	26292	27618	8907
Data>2σ/parameters/restraits	2861/190/0	8112/498/0	7119/464/0	13950/775/8	4636/313/0
R_1[F2>2σ (F2)], wR_2 (F2)	0.0558, 0.1235	0.0426, 0.1014	0.0393, 0.1056	0.472, 0.0844	0.0516, 0.1102
Goodness of fit	1.036	0.951	1.093	0.806	0.821



Scheme 2. Synthetic pathways for compound 1.

larger susceptibility that corresponds to an S = 2 spin system. Notably, the Mn – N bonds in **1Mn** are longer than those seen in **1Fe**.

The 1:1 complex **1Zn** (Fig. 2) has the remainder of the coordination sphere occupied by solvent methanol molecules. **1Zn** adopts an octahedral coordination environment, with three meridonal positions occupied by neutral methanol solvent molecules. The Zn – O bond distances in **1Zn** are 2.193(3), 2.116(4), and 2.157(3) Å, which correlate well with neutral methanol binding to Zn(II). The counter ion in **1Zn**, a perchlorate, is non-coordinating. The compound is in the divalent oxidation state, as evinced by the presence of a counter ion in the crystal structure, bond length distances and by a diamagnetic NMR spectrum observed in **1Zn**. The structure of this compound is very similar to that seen in the Cu(II) complex of **1** reported by Meder and Gade [6].

Table 2
M – N bond distances in compounds **1Mn**, **1Fe**, **1Co**, and **1Zn**.

	M – $N_{indoline}$ (Å)	Mn – $N_{thiazole}$ (Å)
1Mn	1.968(2), 1.967(2)	2.143(2), 2.165(2), 2.134(2), 2.141(2)
1Fe	1.9283(15), 1.9216(16)	1.9849(16), 1.9912(15), 1.9831(15), 1.9707(15)
1Co	1.913(4), 1.931(4)	1.955(4), 1.954(4), 1.962(4), 1.964(4)
1Zn	2.056(4)	2.092(4), 2.096(4)

In conclusion, we present an investigation into the synthesis of the first row transition metal complexes of the 1,3-bis(2-thiazolylimino) isoindoline ligand, **1**. This compound can be readily generated via the reaction of aminothiazole with diiminoisoindoline in butanol solution, resulting in the formation of pure crystals of **1** without phthalocyanine contamination. Compound **1** readily forms complexes with first row transition metal ions in both 1:1 and 2:1 stoichiometries, but in all cases chelates via the nitrogen atoms rather than the thiazole sulfur atoms. As in other bis(2-iminoaryl)isoindoline ligands, compound **1** binds to metal ions in a tridentate, planar fashion. We are continuing

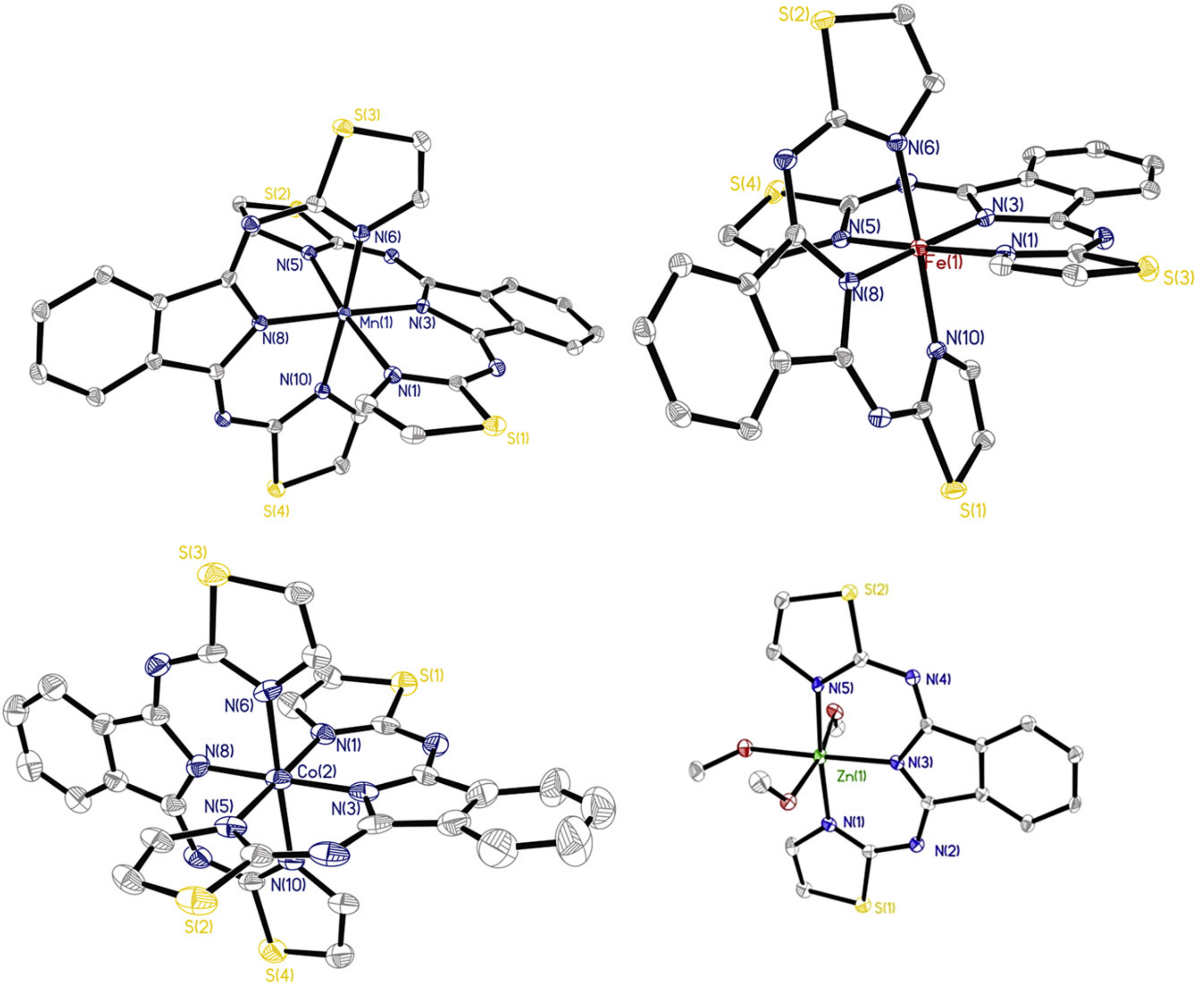


Fig. 2. Structures of **1Mn**, **1Fe**, **1Co**, and **1Zn** with 35% thermal ellipsoids. Hydrogen atoms and anions have been omitted for clarity.

our investigations into isoindoline-based chelates and related macrocycles.

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Appendix A. Supplementary material

CCDC 824820–824824 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary materials related to this article can be found online at doi: 10.1016/j.inoche.2011.08.001.

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