

Research Article

Nickel (II) and Iron (II) Complexes with Azole Derivatives: Synthesis, Crystal Structures and Antifungal Activities

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Two new complexes of nickel (II) with 4-amino-3, 5-bis(pyridyl)-1, 2, 4-triazole (abpt) and iron (II) with 2-(3-phenyl-1H-pyrazole-5-yl) pyridine (phpzpy) have been synthesized and characterized by elemental analysis and IR spectroscopy. The crystal structures of the complexes have been determined by single crystal X-ray diffraction techniques. In the nickel and iron complexes, the ligands are coordinated through nitrogen atoms in bidentate manner. The ligands and their respective complexes have been tested for their antifungal activity against *Aspergillus niger*, *Aspergillus flavus*, and *Candida albicans*. From the study, the complexes showed enhanced activities against the tested organisms compared to the ligands.

1. Introduction

Aromatic nitrogen heterocycles represent an important class of compounds which can act as ligands towards metal ions [1]. Azoles belong to this class and are five-membered heterocyclic ligands containing two or more heteroatoms, one of which must be nitrogen. These compounds have been paid considerable attention due to their wide applicability in medicine [2–4].

Pyrazole and triazole derivatives are subject of many research studies due to their widespread potential biological activities such as antitumour [5, 6], anti-inflammatory [7], antipyretic [8], antiviral [9], antimicrobial [10, 11], anticonvulsant [12], antihistaminic [13], antidepressant [14, 15], insecticides, and fungicides. In coordination chemistry pyrazole- and triazole-derived ligands exhibit various coordination modes and have received considerable attention for the synthesis of transition metal complexes with various nuclearities [16]. Herein we report on the synthesis, structural

determination, and antifungal activities of Ni(II) and Fe(II) complexes of abpt and phpzpy, respectively. The crystal structures of the complexes are described and compared with those of closely related structures.

2. Experimental

2.1. Materials and Physical Measurements. Elemental analysis for carbon, hydrogen, and nitrogen was performed on a Thermo Flash EA-1112 Series CHNS-O Elemental Analyzer. The IR spectra were obtained from KBr pellets in the range 4000–400 cm⁻¹ using a Perkin-Elmer Spectrum 100 FT-IR spectrometer.

2.2. Single Crystal X-Ray Diffraction Analysis and Structure Determination. Suitable single crystals of **1** and **2** were selected and mounted in air onto a loop. The data collection for **1** and **2** was carried out with a Bruker DUO APEX II CCD

diffractometer at 173(2) K using an Oxford cryostream 700. Data reduction and cell refinement were performed using SAINT-Plus, [17–21] and the space group was determined from systematic absences by XPREP [22] and further justified by the refinement results. Graphite-monochromated Mo K α ($\lambda = 0.71073$ Å) radiation was used in both cases. The X-ray diffraction data have been corrected for Lorentz-polarization factor and scaled for absorption effects by multiscan using SADABS [23]. The structures were solved by direct methods, implemented in SHELXS-97 [24]. Refinement procedures by full-matrix least-squares methods based on F^2 values against all reflections have been performed by SHELXL-97, [24] including anisotropic displacement parameters for all non-H atoms. The positions of hydrogen atoms belonging to the carbon atoms Csp² were geometrically optimized by applying a riding model. Calculations concerning the molecular geometry, the affirmation of chosen space groups, and the analysis of hydrogen bonds were performed with PLATON [25]. The molecular graphics were done with ORTEP-3[26] and Mercury (version 3.0) [27]. The crystal parameters, data collection, and refinement results for **1** and **2** are summarized in Table 1.

2.3. Antifungal Activity. The synthesized abpt, phpzpy, and their metal complexes **1** and **2** were screened *in vitro* for their antifungal activity against three fungi: *Aspergillus niger*, *Aspergillus flavus*, and *Candida albicans* and evaluated by poisoned food technique [28, 29]. The molds were grown on Sabouraud dextrose agar (SDA) at 25°C for 7 days and used as inocula. DMSO was used as the negative control while fluconazole was used as the positive control. The experiments were performed in triplicates. Diameters of fungal colonies were measured and expressed as percent mycelial inhibition:

$$\text{percent inhibition of mycelial growth} = \frac{(dc - dt)}{dc} \times 100, \quad (1)$$

where dc is average diameter of fungal colony in negative control sets and dt is the average diameter fungal colony in experimental sets.

2.4. Synthesis of Ligands. The ligand 4-amino-3, 5-bis(2-pyridyl)-1,2, 4-triazole (abpt) was prepared in two steps from commercially available precursors, as previously described [30–32], while its counterpart 2-(3-phenyl-1H-pyrazole-5-yl)pyridine(phppyz) was equally synthesized as previously reported [33].

2.5. Synthesis of $[Ni(abpt)_2(OH)_2]ClO_4^{2-}$ (1**).** To a solution of 4-amino-3, 5-bis(pyridyl)-1,2,4-triazole (abpt) (238 mg, 1 mmol) in methanol (20 cm³) Ni(ClO₄) \cdot 6H₂O (0.375 mg, 1 mmol) was added in water/methanol (1 : 1) solution (10 cm³) with continuous stirring for 2 h. The product was filtered and allowed to evaporate slowly at room temperature resulting the formation of dark red crystals suitable for single crystal X-ray diffraction studies after one week. *Yield* 80%. *Anal. Calcd.*: C, 64.17; H, 2.67; N, 3.74. *Found*: C, 64.00; H, 2.69; N, 3.44%. IR

absorption bands (KBr, cm⁻¹): 3387s, 3260s, 2108m, 2070s, 2041vs, 1608s, 1589s, 1433 and 1088w, 777s, 731m, 633s.

2.6. Synthesis of $[Fe(phppyz)_2(NCS)_2]$ (2**).** To a methanolic solution (15 mL) of $[Fe(H_2O)_6](ClO_4)_2$ (153 mg; 0.42 mmol) (and a pinch of ascorbic acid) a solution of KNCS (82 mg; 0.84 mmol) was added in the same solvent (15 mL) under nitrogen. The mixture was stirred for 15 min then filtered (to remove KClO₄) via a cannula into a schlenk containing a solution of phpzpy (18 mg; 0.84 mmol) in methanol. Water (5 mL) was added, and the solution was stirred for 1 h at room temperature, then left to evaporate under nitrogen. Single crystal suitable for X-ray diffraction was obtained after two days as yellow block. *Yield* 75%. *Anal. Calcd.*: C, 67.94; H, 4.15; N, 5.28. *Found*: C, 67.93; H, 3.95; N, 5.63%. IR absorption bands (KBr, cm⁻¹): 3205sh, 3053s, 2084s, 1615s, 1571m, 1510w, 1459w, 1432m, 1291w, 1250w, 1061w, 968w, 927w, 772s, 707w, 636w, 471w.

3. Results and Discussion

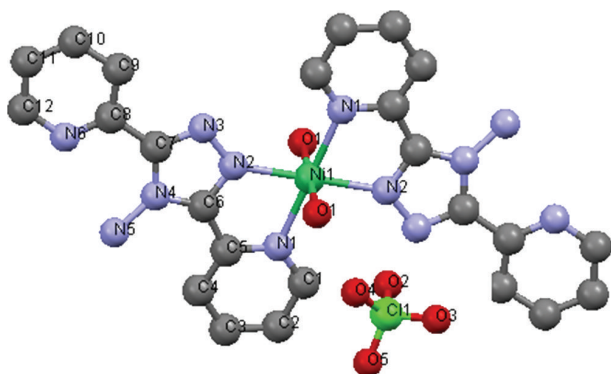
3.1. Antifungal Activity. The ligands abpt and phpzpy, their complexes, standard drug (fluconazole), and DMSO solvent were screened separately for their antifungal activity against *Aspergillus flavus*, *Aspergillus niger*, and *Candida albicans*. The ligands were found to show antifungal activity, and their metal complexes show enhanced activity compared to the free ligands. Of the four chemical compounds screened for their antifungal activity, three of them showed more than 50% inhibition of mycelial growth against the three fungal strains while one showed less than 50% mycelial growth against the fungi compared to the standard drug with greater than 70% inhibition (Table 3). The overtone's concept [34] and Tweedy's chelation theory [35] can be used to explain the enhancement in antifungal activity of the metal complexes. Chelation considerably reduces the polarity of the metal ion because of partial sharing of its positive charge with the donor group and possible π -electron delocalization within the entire chelate ring system that is formed during coordination. Such chelation could enhance the lipophilic character of the central metal atom and hence increase the hydrophobic character and liposolubility of the complex favouring its permeation through the lipid layers of the cell membrane.

3.2. Description of the Crystal Structures. The structure of complex **1** with the atomic numbering scheme is shown in Figure 1. The bond lengths and bond angles for the complex **1** are listed in Table 2. Complex **1** crystallizes in the monoclinic P2₁/n space group, and the coordination geometry around the Ni(II) center can be described as a six-coordinated distorted octahedron where four nitrogen atoms from two bidentate abpt ligands and two oxygen atoms from water molecule occupy the six coordination with the chlorate anion as the counter ion in the outer sphere. The average Cl–O bond distance is 1.37(2) Å.

The Ni–N_{1py} and Ni–N_{2tr} bond length values are 2.105(8) Å and 2.039(7) Å respectively, while the Ni–O₁ bond

TABLE 1: Crystal data and structure refinement for compounds **1** and **2**.

Compound	(1)	(2)
Empirical formula	C ₂₀ H ₁₀ ClNNiO	C ₃₀ H ₂₂ FeN ₂ S ₂
FW	374.14	529.97
<i>T</i> (K)	293(2)	293(2)
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>C</i> 2/ <i>c</i>
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Unit cell dimensions		
<i>a</i> (Å)	9.937(2)	16.839(3)
<i>b</i> (Å)	14.363(3)	9.671(19)
<i>c</i> (Å)	10.9218(3)	18.496(6)
<i>V</i> (Å ³)	1532.35(8)	2853.78(18)
<i>Z</i>	4	4
<i>D_x</i> (g/cm ⁻³)	1.624	1.361
<i>μ</i> (mm ⁻¹)	0.092	0.091
<i>F</i> (000)	532	528
Crystal size (mm ³)	0.20 × 0.25 × 0.13	0.20 × 0.20 × 0.25
<i>θ</i> range (deg)	1.77–27.48	1.60–27.48
Index range (<i>h, k, l</i>)	−10/10, 13/12, −28/28	−8/8, −8/8, −25/29
Reflection collected	4896	4791
Independent reflections	2095	2144
(<i>R</i> _{int})	0.1111	0.0187
Data/restraints/parameter	3501/1/224	2501/0/187
Goodness-of-fit on <i>F</i> ²	0.918	1.034
Final <i>R</i> indices [<i>I</i> > 2σ > (<i>I</i>)]	<i>R</i> ₁ = 0.1435, <i>wR</i> ₂ = 0.4235	<i>R</i> ₁ = 0.0536, <i>wR</i> ₂ = 0.1231
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.1604, <i>wR</i> ₂ = 0.4365	<i>R</i> ₁ = 0.0865, <i>wR</i> ₂ = 0.1335
Largest diff. peak and hole (e Å ⁻³)	0.243 and −0.275	0.663 and −0.557

FIGURE 1: Molecular diagram of complex salt **1** with the atom numbering scheme (hydrogen atoms are omitted for clarity)

length is 2.109(6) Å which are similar to those of other nickel complexes reported elsewhere [30, 36, 37]. The Ni–N

TABLE 2: Selected bond lengths (Å) and bond angles (°) of **1** and **2**.

Complex (1)			
Ni(1)–O(1)	2.109(6)	O(1)–Ni(1)–N(1)	89.8(3)
Ni(1)–N(1)	2.105(8)	O(1)–Ni(1)–N(2)	90.4(3)
Ni(1)–N(2)	2.309(7)	O(1)–Ni(1)–O(1)	180.0(2)
		N(1)–Ni(1)–N(1)	180.0(3)
		N(1)–Ni(1)–N(2)	100.8(3)
		N(2)–Ni(1)–N(2)	180.0(3)
Complex (2)			
Fe(1)–N(2)	2.133(2)	N(2)–Fe(1)–N(1)	73.66(8)
Fe(1)–N(4)	2.107(3)	N(1)–Fe(1)–N(2)	96.87(9)
Fe(1)–N(1)	2.250(2)	N(2)–Fe(1)–N(4)	87.61(1)
N(4)–C(008)	1.159(4)	N(4)–Fe(1)–N(4)	99.90(1)
S(2)–C(008)	1.618(4)	N(4)–Fe(1)–N(1)	90.90(1)
N(2)–N(3)	1.351(3)	N(4)–Fe(1)–N(2)	87.60(1)

Symmetry transformations used to generate equivalent atoms for (**1**): *x, y, z, 1/2 − z, −x, −y, −z, 1/2 + x, 1/2 − y, 1/2 + z*. (**2**): *−x, y, 1/2 − z, 1/2 + y, z, 1/2 − x, x, −y, −z, 1/2 + z, 1/2 − y*.

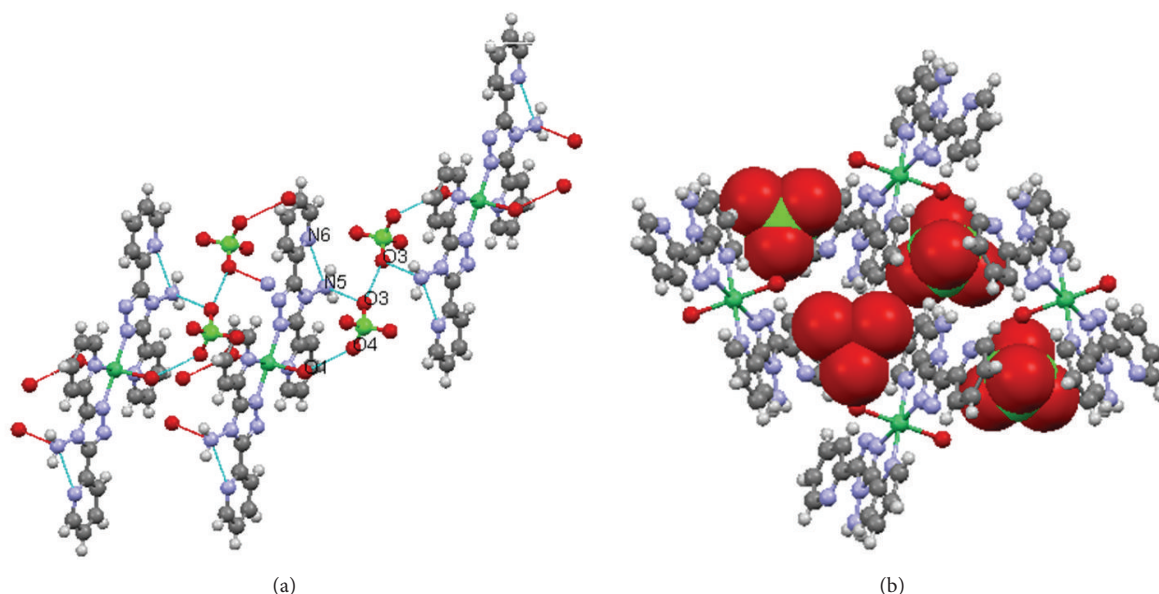


FIGURE 2: (a) Intra- and intermolecular hydrogen bond of complex 1. (b) Packing diagram of the complex salt 1 where chlorate anions are shown in space-filling model.

TABLE 3: Antifungal activity of synthesized compounds.

Compound	Mycelial growth inhibition (%)		
	<i>A. niger</i>	<i>A. flavus</i>	<i>C. albicans</i>
abpt	54.2	57.2	55.6
phpzpy	49.3	48.6	49.7
[Ni(abpt)(OH ₂) ₂]ClO ₄	61.3	60.6	59.6
[Fe(phpzpy) ₂ (SCN) ₂]	58.2	57.8	57.4
Fluconazole	81.1	77.7	79.5

distances of 2.039(7) Å to 2.105(8) Å are considerably shorter than the Ni–O1 of 2.109(7) Å indicating the stronger ability of the nitrogen to bond to the Ni than the oxygen atom. Furthermore the longer Ni–N_{py} distance compared to its Ni–N_{trz} counterpart is consistent with other systems of this ligand type [38]. The two water molecules occupy the apical position whereas; the two triazole ligands occupy the equatorial plane. The bond angles between apical axis and equatorial plane in complex 1 vary from 90°, indicating distortion of the octahedral structure. The N1–Ni1–N2 bond angles varies from 51.2(2)° to 79.2(3)° while the O1–Ni1–N1 bond angle is 89.8(3)° and O1–Ni–N2 is 90.4(3)°. Furthermore the O1–Ni–O1 bond angle is 180(2)° which are all comparable to other nickel (II) complexes with similar ligands [36, 37]. There exists the intra molecular and intermolecular hydrogen bond in the complex 1. The intra molecular hydrogen bond exists between N6–N5–H and the intermolecular bond between O4···O1–H and O3···N5–H as shown in Figure 2(a). The chlorate anions are held in the vacant space between the abpt ligand wings of two complex cations by O3···N5–H and O3···O3 and O4···O1–H with bond distances of 2.87, 3.036 and 2.309 Å respectively

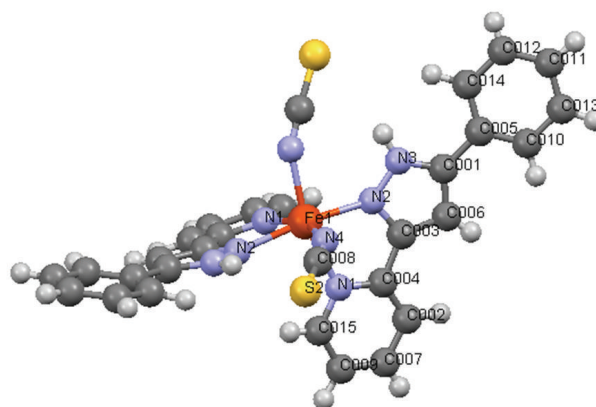


FIGURE 3: Molecular diagram of complex 2 with the atom-numbering scheme.

as shown in Figure 2(b). An electrostatic interaction O3···O3 with bond distance 3.04(2) Å is observed.

The structure of the complex 2 with the atom numbering scheme is depicted in Figure 3. The bond lengths and bond angles are listed in Table 2. This complex crystallizes in the monoclinic C2/c space group. The coordination geometry around the Fe(II) is a six coordinate distorted octahedron where four nitrogen atoms from the two bidentate neutral phpzpy ligand and two nitrogen atoms from the thiocyanate ligands occupy the six coordination sites. The bond distance of Fe–N_{py} = 2.250(2) Å is longer than that of the Fe–N_{pz} = 2.13(2) Å as would be expected for ligands of this type [38], whereas the Fe–N_{thio} = 2.107(3) Å is considerably shorter than the Fe–N_{pz} and Fe–N_{py} counterpart due to the stronger ability of the thiocyanate ion to bind the Fe in comparison

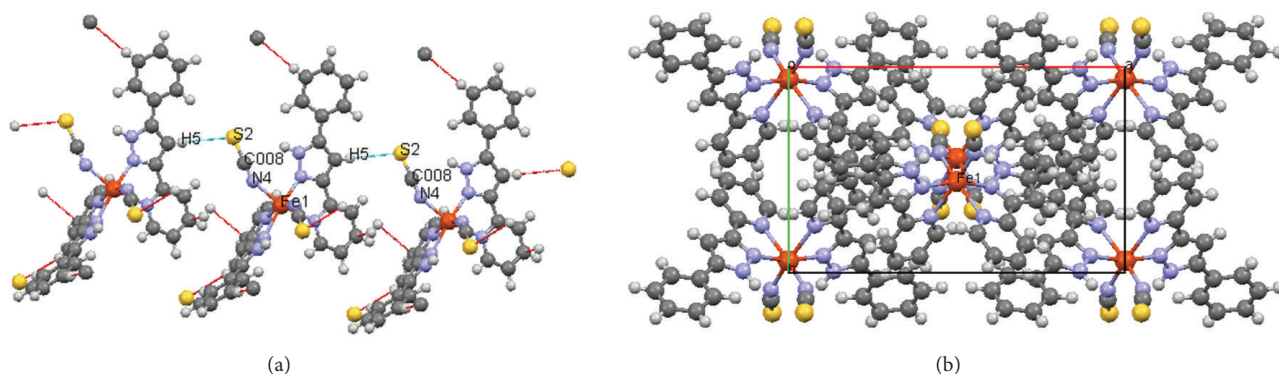


FIGURE 4: (a) Intermolecular hydrogen bond of complex 2. (b) Packing diagram of complex 2 along the *c*-axis.

to the neutral bidentate ligand. The N4–C008 bond distance is 1.159(4) Å, and S2–C008 distance is 1.618(4) Å. These observed C–N and C–S bond length values which fall in the 1.133 Å to 1.159(4) Å and 1.612–1.168(4) Å range, for complex 2, have been reported in other thiocyanato complexes [39].

The ligand phpzpy is not completely planar. The pyridyl and phenyl groups are slightly twisted with respect to the pyrazole. The angles between the rings py–pz = 27.84(7)°, py–ph = 63.51(6)°, and pz–ph = 19.97(5)° in the complex. The N2–Fe1–N1 and N2–Fe1–N4 bond angles are 73.66(8)° and 87.64(1)°. Furthermore the N4–Fe1–N4, N4–Fe1–N1, and N4–Fe1–N2 are 99.9(1)°, 90.9(1)°, and 87.6(1)°, respectively. In the crystal packing (Figure 4(a)) intermolecular hydrogen bonds C008–S1...H5 exist in the complex.

4. Conclusion

We have synthesized and characterized by elemental analysis, IR, and XRD spectroscopic techniques Ni(II) and Fe(II) complexes with azole derivatives abpt and phppyz, respectively. The complexes and their ligands have been tested for their antifungal activity against three fungal strains *A. niger*, *A. flavus*, and *C. albicans*, and the complexes have shown enhanced activity compared to their parent ligands.

5. Further Material

Crystallographic data for the structures reported in this paper have been deposited with Cambridge Crystallographic Data Center as supplementary publication no. CCDC-875789 and 875790. Copies of the data can be obtained free of charge from CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax (44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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