Bull. Chem. Soc. Jpn. Vol. 84, No. 2, 205–210 (2011)

Synthesis and Characterization of 3d Metal Complexes Based on 1-(4-Nitrophenyl)imidazole

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Synthesis and characterization of complexes with formulations $[M(nopi)_2Cl_2]$ ($M = Co$, **1**; Ni, **3**; Cu, **6**; Zn, **9**), $[M(nopi)_6](X)_2$ ($X^- = NO_3^-$, $M = Co$, **2**; Ni, **4**; Zn, **10**; $X^- = ClO_4^-$, $M = Ni$, **5**; Cu, **8**; Zn, **11**) and $[Cu(nopi)_4(NO_3)_2]$ (**7**) imparting 1-(4-nitrophenyl)imidazole (nopi) have been described. The complexes have been characterized by elemental analyses and spectral (IR, ^1H NMR, electronic absorption and emission) studies. Molecular structures of **7** and **9** have been determined crystallographically. Weak interaction studies on **7** and **9** revealed the presence of various interesting motifs resulting from C–H···N, C–H···Cl, and π–π stacking interactions. Temperature-dependent (313–373 K) pressed pellet conductivity and activation energy calculations from the plot of ln σ vs. $1/T$ suggested semiconducting behavior of **2**, **6**, and **7**.

Rational design and synthesis of supramolecular coordination networks have seen a large surge during the past couple of decades by virtue of possible applications in various areas.[1] A large number of networks have been successfully designed and synthesized through judicious choice of the ligands and metal ions.[2] Rational design based on covalent or supramolecular interactions is a key step in self-assembly supramolecular chemistry.[3] It is well established that noncovalent interactions including electrostatic and hydrogen bonding play a vital role in constructing supramolecular systems.[4] The self-assembly of metal–organic frameworks is greatly influenced by factors such as the solvent system, pH of the solution, geometric requirements of the metal ions, and counter ions.[5] Further, several forces such as coordination bonding, hydrogen bonding, π–π stacking, and electrostatic interactions have been recognized and used in the construction of extended inorganic networks. Among these, coordination bonding and hydrogen-bonding interactions are most important. One synthetic strategy generally employed in this area is controlled assembly of donor and acceptor building blocks to generate supramolecular buildings.[6,7] High directionality of hydrogen bonds present in supramolecular architectures makes them useful in the designing of functional materials with controlled physicochemical, catalytic, and optical properties.[3a–3c,8]

Further, imidazole and the ligands based on it have proven to be very useful. Good coordination ability, diverse coordination modes, and bridging ability of the imidazole and its derivatives have prompted their use in the construction of extended solids.[7] In this context, 1-(4-cyanophenyl)imidazole (cpi) has attracted considerable current attention.[7a,7b] Substitution of the cyanophenyl group by nitrophenyl may be useful in fine tuning the luminescent, catalytic and other properties of the resulting systems based on 1-(4-nitrophenyl)imidazole (nopi). In continuation of our previous studies on metal complexes based on substituted phenylimidazole ligands, we have examined reactivity of nopi with various metal salts and have isolated self-assembled systems resulting from weak bonding interactions.[7] Through this work we present the synthesis and characterization of complexes with the formulations $[M(nopi)_2Cl_2]$ ($M = Co$, **1**; Ni, **3**; Cu, **6**; Zn, **9**) and $[M(nopi)_6](X)_2$ ($X^- = NO_3^-$, $M = Co$, **2**; Ni, **4**; Zn, **10**; $X^- = ClO_4^-$, $M = Ni$, **5**; Cu, **8**; Zn, **11**) and $[Cu(nopi)_4(NO_3)_2]$ (**7**) and single-crystal X-ray structures of **7** and **9**. Also, we decribe herein results on weak bonding interactions in **7** and **9**, luminescence behavior of the complexes and pressed pellet conductivity measurements on **2**, **6**, and **7**.

Experimental

Reagents. All the synthetic manipulations were performed under nitrogen atmosphere in de-aerated solvents. The solvents were purified rigorously by standard procedures prior to their use.[9] Metal salts $CoCl_2$, $ZnCl_2$, $CuCl_2$, $NiCl_2\cdot6H_2O$, $Co(NO_3)_2\cdot6H_2O$, $Ni(NO_3)_2\cdot6H_2O$, $Cu(NO_3)_2\cdot3H_2O$, $Ni(ClO_4)_2\cdot6H_2O$, $Cu(ClO_4)_2\cdot6H_2O$, $Zn(ClO_4)_2\cdot6H_2O$, and other reagents were procured from Sigma-Aldrich and were used as received without further purifications. 1-(4-Nitrophenyl)imidazole (nopi) has been prepared by literature procedure using imidazole and 4-fluoronitrobenzene (all Aldrich).[10]

Instrumentation and General Methods. Elemental analyses for C, H, N in the complexes were performed on an Exter CE-440 CHN analyzer. IR in KBr discs and electronic spectra in DMSO solution were recorded on a Shimadzu-8201PC and Shimadzu UV-1700 spectrophotometers, respectively. ^1H NMR spectra of **9**–**11** were acquired in DMSO-d_6 on a JEOL 300 MHz NMR instrument using TMS as an internal reference. Pressed pellet conductivity of the complexes was measured on a Keithley 236 Source Measure Unit by employing a conventional two probe technique. Emission spectra were recorded on a Varian Carry Eclipse Fluorescence spectrophotometer at room temperature.

Synthesis. The following general procedure was employed for the synthesis of all the complexes: In a typical reaction,

Published on the web February 4, 2011; doi:10.1246/bcsj.20100154

respective metal salts (1.0 mM) were treated with 1-(4-nitrophenyl)imidazole (nopi) (2.0 mM) in ethanol–water mixture (1:4 v/v). After stirring well, the reaction mixture was allowed to heat in a sealed tube at 120 °C for 72 h and the resulting solution was allowed to cool slowly to ambient temperature. Crystalline products were separated from the reaction mixture in a couple of days. It was separated by filtration, washed several times with water, ethanol, and diethyl ether and dried in air. Selected characterization data of the complexes are given below.

[Co(nopi)$_2$Cl$_2$] (1): Yield of ca. 65% (0.330 g). MW: 508.19, Anal. Calcd for **1** ($C_{18}H_{14}N_6O_4Cl_2Co$): C, 42.54; H, 2.78; N, 16.54%. Found: C, 42.39; H, 2.46; N, 16.33%. IR (KBr pellets, cm^{-1}): 3086 (s), 1597 (vs), 1513 (vs), 1433 (s), 1340 (vs), 1305 (vs), 1270 (s), 1200 (w), 1112 (s), 1064 (s), 1008 (w), 958 (w), 844 (vs), 747 (s), 622 (w), 506 (w). λ_{max}/nm (λ_{ex}/nm) = 395 (284).

[Co(nopi)$_6$](NO$_3$)$_2$ (2): Yield of ca. 67% (0.294 g). MW: 1317.98. Anal. Calcd for **2** ($C_{54}H_{42}N_{20}O_{18}Co$): C, 49.21; H, 3.21; N, 21.25%. Found: C, 49.13; H, 3.19; N, 21.18%. IR (KBr pellets, cm^{-1}): 3484 (vbr), 3123 (s), 2880 (w), 1602 (vs), 1526 (vs), 1458 (s), 1398 (s), 1271 (w), 1218 (w), 1176 (s), 1126 (s), 1064 (s), 958 (w), 828 (vs), 751 (s), 646 (w), 514 (s). λ_{max}/nm (λ_{ex}/nm) = 392 (275).

[Ni(nopi)$_2$Cl$_2$] (3): Yield of ca. 67% (0.340 g). MW: 507.94. Anal. Calcd for **3** ($C_{18}H_{14}N_6O_4Cl_2Ni$): C, 42.56; H, 2.78; N, 16.55%. Found: C, 42.31; H, 2.86; N, 16.63%. IR (KBr pellets, cm^{-1}): 3450, 3084, 1596, 1514, 1433, 1339, 1305, 1270, 1200, 1111, 1065, 1009, 957, 846, 745, 688, 621, 506. λ_{max}, nm (λ_{ex}/nm) = 393 (269).

[Ni(nopi)$_6$](NO$_3$)$_2$ (4): Yield of ca. 64% (0.281 g). MW: 1317.74. Anal. Calcd for **4** ($C_{54}H_{42}N_{20}O_{18}Ni$): C, 49.22; H, 3.21; N, 21.26%. Found: C, 49.17; H, 3.15; N, 21.18%. IR (KBr pellets, cm^{-1}): 3450, 3123, 1599 (vs), 1520 (s), 1382 (br), 1343, 1305, 1112 (s), 1060 (s), 962 (w), 855, 750 (s), 684 (w), 657 (w), 510. λ_{max}/nm (λ_{ex}/nm) = 387 (289).

[Ni(nopi)$_6$](ClO$_4$)$_2$ (5): Yield of ca. 61% (0.283 g). MW: 1392.63. Anal. Calcd for **5** ($C_{54}H_{42}N_{18}O_{20}Cl_2Ni$): C, 46.57; H, 3.04; N, 18.10%. Found: C, 46.06; H, 2.99; N, 18.30%. IR (KBr pellets, cm^{-1}): 3468, 3123, 2930, 1600 (vs), 1522 (s), 1381 (br), 1343, 1307, 1263 (vs), 1185 (w), 1112 (vs), 1064, 963, 854, 784, 685 (w), 651 (w), 509. λ_{max}/nm (λ_{ex}/nm) = 383 (285).

[Cu(nopi)$_2$Cl$_2$] (6): Yield of ca. 65% (0.333 g). MW: 512.80. Anal. Calcd for **6** ($C_{18}H_{14}N_6O_4Cl_2Cu$): C, 42.16; H, 2.75; N, 16.39%. Found: C, 42.05; H, 2.66; N, 16.43%. IR (KBr pellets, cm^{-1}): 3454, 3125, 2918, 1602 (vs), 1517, 1489, 1376 (s), 1304 (vs), 1213, 1168, 1120 (w), 1061 (s), 958 (w), 829 (vs), 759 (s), 478 (w). λ_{max}/nm (λ_{ex}/nm) = 393 (292).

[Cu(nopi)$_4$(NO$_3$)$_2$] (7): Yield of ca. 68% (0.321 g). MW: 944.25. Anal. Calcd for **7** ($C_{36}H_{28}N_{14}O_{14}Cu$): C, 45.79; H, 2.99; N, 20.77%. Found: C, 45.23; H, 3.09; N, 20.28%. IR (KBr pellets, cm^{-1}): 3448, 3121, 1599 (vs), 1518 (s), 1383 (br), 1343, 1304, 1113 (s), 1060 (s), 962 (w), 853, 750 (s), 688 (w), 657 (w), 510.

[Cu(nopi)$_6$](ClO$_4$)$_2$ (8): Yield of ca. 61% (0.284 g). MW: 1397.49. Anal. Calcd for **8** ($C_{54}H_{42}N_{18}O_{20}Cl_2Cu$): C, 46.41; H, 3.03; N, 18.04%. Found: C, 46.06; H, 3.12; N, 17.94%. IR (KBr pellets, cm^{-1}): 3944, 3118, 2945, 1598 (vs), 1517 (s), 1382 (br), 1343, 1305 (vs), 1265 (vs), 1186 (w), 1115, 1063, 963 (w), 853, 783, 684, 614 (s), 520.

[Zn(nopi)$_2$Cl$_2$] (9): Yield of ca. 59% (0.303 g). MW: 514.63. Anal. Calcd for **9** ($C_{18}H_{14}N_6O_4Cl_2Zn$): C, 42.01; H, 2.74; N, 16.33%. Found: C, 41.86; H, 2.66; N, 16.04%. IR (KBr cm^{-1}): 3421, 3221, 1600 (vs), 1522 (vs), 1385 (s), 1338, 1310 (vs), 1260 (s), 1189 (w), 1059 (s), 962 (w), 825 (vs), 761 (s), 476. λ_{max}/nm (λ_{ex}/nm) = 381 (298). ^{1}H NMR (DMSO): δ 7.17 (s, 1H), 7.93 (d, 3H, J = 7.2 Hz), 8.01 (d, 2H, J = 6.6 Hz), 8.46 (s, 1H).

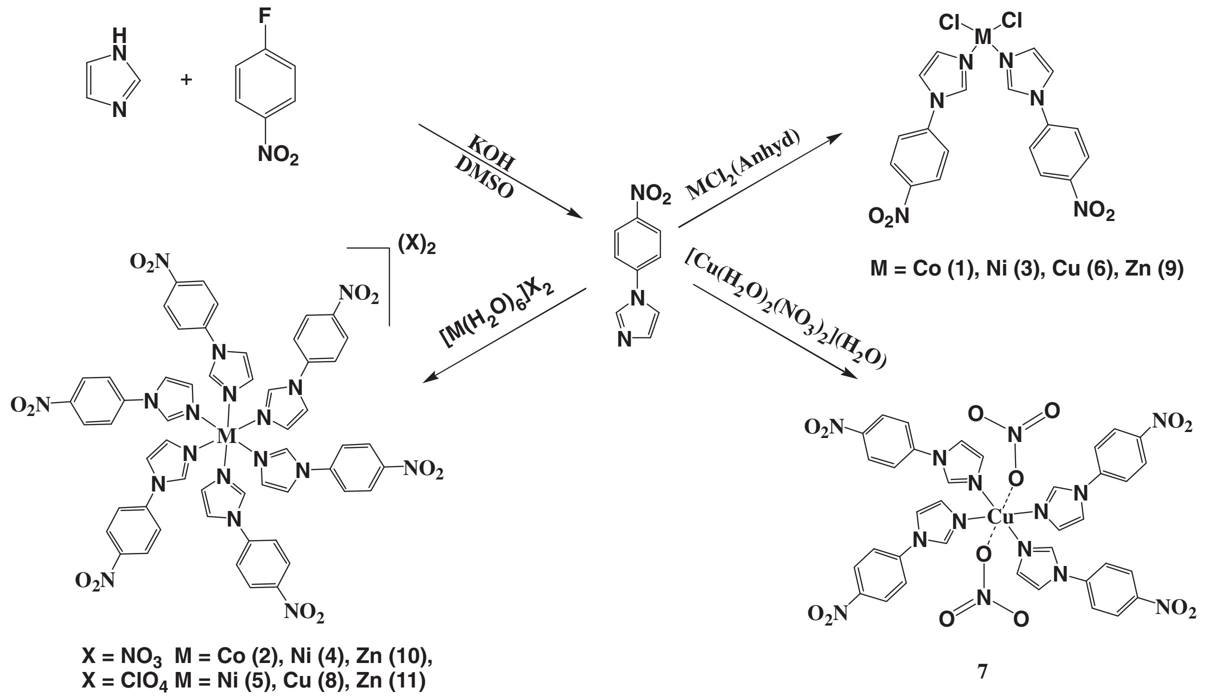
[Zn(nopi)$_6$](NO$_3$)$_2$ (10): Yield of ca. 60% (0.265 g). MW: 1324.43 Anal. Calcd for **10** ($C_{54}H_{42}N_{20}O_{18}Zn$): C, 48.97; H, 3.20; N, 21.15%. Found: C, 48.43; H, 3.05; N, 21.08%. IR (KBr pellets, cm^{-1}): 3470, 3123 (s), 2929, 2851, 1600 (vs), 1521 (s), 1381 (br), 1340, 1307, 1263, 1187 (s), 1111 (s), 1064 (s), 963 (w), 853, 748 (s), 685, 650, 507. λ_{max}/nm (λ_{ex}/nm) = 378 (288).^{1}H NMR (DMSO): δ 7.19 (s, 1H), 7.99 (d, 3H, J = 9.6 Hz), 8.37 (d, 2H, J = 8.7 Hz), 8.50 (s, 1H).

[Zn(nopi)$_6$](ClO$_4$)$_2$ (11): Yield of ca. 58% (0.270 g). MW: 1399.32. Anal. Calcd for **11** ($C_{54}H_{42}N_{18}O_{20}Cl_2Zn$): C, 46.35; H, 3.03; N, 18.02%. Found: C, 45.99; H, 3.09; N, 18.24%. IR (KBr pellets, cm^{-1}): 3317 (vbr), 3212 (s), 3121 (br), 2230.9 (vs), 1609 (vs), 1521 (s), 1425 (s), 1373 (br), 1308 (vs), 1268 (vs), 1188 (w), 1118 (s), 1065 (vs), 962 (w), 838 (s), 753 (s), 655 (w), 552 (w). λ_{max}/nm (λ_{ex}/nm) = 369 (278).^{1}H NMR (DMSO): δ 7.28 (s, 1H), 8.03 (d, 3H, J = 8.7 Hz), 8.38 (d, 2H, J = 8.7 Hz), 8.66 (s, 1H).

Crystallographic Data. Crystals suitable for single-crystal X-ray diffraction analyses for **7** and **9** were obtained directly from the reaction mixture after cooling. Preliminary data on the space group and unit cell dimensions as well as intensity data were collected for complex **7** on OXFORD DIFFRACTION X CAUBER-S and **9** on a BRUKER SMART APEX diffractometer using graphite monochromatized Mo Kα radiation. The crystal orientation, cell refinement, and intensity measurements were made using the program CAD-4 PC. The structures were solved by direct methods using SHELXS-97,[11] and full-matrix least-squares refinement against F^2 using SHELXL-97.[12] Non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were geometrically fixed and allowed to refine using a riding model. PLATON was used for analyzing the interaction and stacking distances.[13] CCDC-776179 for **9** and -776180 for **7** 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.

Crystallographic Data for 9: Formula: $C_{18}H_{14}Cl_2N_6O_4Zn$, MW: 514.62, specimen 0.16 mm × 0.14 mm × 0.12 mm, monoclinic, space group $P2_1/n$, $a = 7.6352(15)$ Å, $b = 17.233(3)$ Å, $c = 16.144(3)$ Å, $\beta = 93.27(3)°$, $V = 2120.7(7)$ Å^3, $Z = 4$, $D_{calcd} = 1.612$ g cm^{-3}, $F(000) = 1040$, $\mu = 1.448$ mm^{-1}, T/K = 153(2), $\lambda = 0.71073$ Å, No. of reflection/parameters = 4827/280, R(all) = 0.0769, $R[I > 2\sigma(I)] = 0.0389$, $wR2$(all) = 0.0857, $wR2$ $[I > 2\sigma(I)] = 0.0714$, $GOF = 1.015$.

Crystallographic Data for 7: Formula: $C_{36}H_{28}CuN_{14}O_{14}$, MW: 944.25, specimen 0.23 mm × 0.17 mm × 0.15 mm, triclinic space group $P\bar{1}$, $a = 8.7913(14)$ Å, $b = 14.2033(17)$ Å, $c = 15.803(2)$ Å, $\alpha = 92.753(10)°$, $\beta = 93.600(12)°$, $\gamma = 94.014(12)°$, $V = 1961.8(5)$ Å^3, $Z = 2$, $D_{calcd} = 1.599$ g cm^{-3},



$F(000) = 966$, $\mu = 0.646\,\text{mm}^{-1}$, $T/\text{K} = 150(2)$, $\lambda = 0.71073$ Å, No. of reflection/parameters $= 6863/586$, $R(\text{all}) = 0.0863$, $R[I > 2\sigma(I)] = 0.0521$, $wR2 = 0.1196$, $wR2[I > 2\sigma(I)] = 0.1088$, $GOF = 0.950$.

Results and Discussion

All the complexes have been prepared by a general procedure wherein respective metal salts (1.0 mmol) and nopi (2.0 mmol) were heated in water–ethanol mixture (10 mL, 4:1) in a sealed tube at 120 °C. Upon cooling to room temperature diffraction quality crystals of **7** and **9** were directly obtained from the reaction mixture. A simple scheme showing the synthesis of complexes is depicted in Scheme 1. Interestingly, reaction of the metal salts with nopi afforded three types of complexes (i) tetrahedral complexes of the formulations [M(nopi)$_2$Cl$_2$], (ii) octahedral complexes [M(nopi)$_6$](X)$_2$, and (iii) square-planar complexes of the type [M(nopi)$_4$(NO$_3$)$_2$], which was obtained only in the case of copper. These observations are consistent with our earlier reports.[7a,7b] The complexes under investigation are air-stable solids, insoluble in common organic solvents like dichloromethane, methanol, ethanol, hexane, diethyl ether, acetone, chloroform, benzene, etc. and are soluble in solvents with high dielectric constant e.g., DMF, DMSO, acetonitrile, etc.

Characterization of the complexes has been achieved by elemental analyses and spectral studies. Selected characterization data are summarized in the experimental section.

Infrared spectra of the respective complexes exhibited characteristic bands due to –NO$_2$ of the nitrophenyl moiety along with imidazole ring vibrations at 1339 and $\approx$1598 cm^{-1}, respectively. The bands corresponding to imidazole ring vibrations appeared at $\approx$1600 cm^{-1} while that in the free nopi appears at 1610 cm^{-1}.[7a,7b] A shift in the position of ν(C=N) suggested linkage of nopi to the metal center through imidazole nitrogen. In the ^{1}H NMR spectra of zinc based complexes **9**–**11**, the phenyl ring protons displayed a significant shift and resonated between $\approx$7.2–8.6 ppm (Figure 1). Integral intensity and shift in the position of various signals suggested the coordination of nopi with respective metal centers.

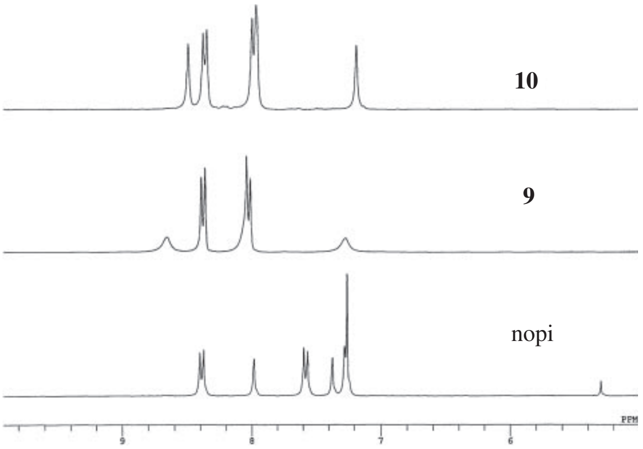


Figure 1. Overlay NMR spectra of nopi (in CHCl$_3$), **9**, and **10** (in DMSO).

Single-Crystal X-ray Diffraction Studies. The structure of tetrahedral complexes of the type [M(nopi)$_2$Cl$_2$] **1**, **3**, **6**, and **9** have been verified by single-crystal X-ray diffraction analyses of the representative complex **9**. Selected crystallographic data are summarized in the crystallographic section and geometric parameters are shown below in Figure 2. Complex **9** crystallizes in a monoclinic system having $P2_1/n$ space group. In this complex coordination geometry about the Zn center is distorted tetrahedral with N$_2$Cl$_2$ donor groups which is analogous to that observed in [Zn(cpi)$_2$Cl$_2$] (cpi: 1-(4-cyanophenyl)imidazole).[7b] Two of the coordination sites about the

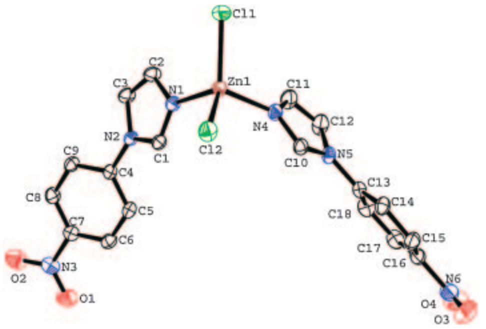


Figure 2. Ellipsoid view of **9** at 30% probability (H atoms excluded for clarity): Selected bond length/Å and angles/°: Zn(1)–N(1) = 2.031(2), Zn(1)–N(4) = 2.020(2), Zn(1)–Cl(1) = 2.2166(10), Zn(1)–Cl(2) = 2.2117(10), N(4)–Zn(1)–N(1) = 102.16(10), N(4)–Zn(1)–Cl(2) = 106.84(7), N(1)–Zn(1)–Cl(2) = 109.64(7), N(4)–Zn(1)–Cl(1) = 109.86(8), N(1)–Zn(1)–Cl(1) = 105.38(7), Cl(2)–Zn(1)–Cl(1) = 121.33(4).

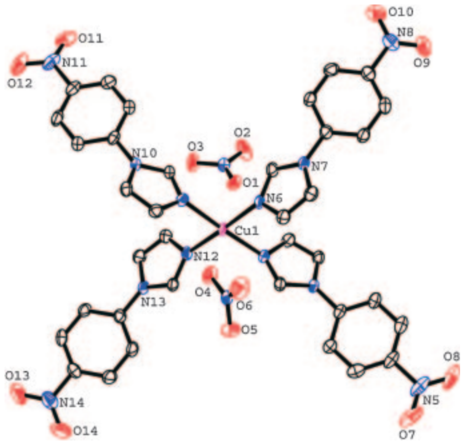


Figure 3. ORTEP view of **7** at 30% probability of thermal ellipsoids (H atoms excluded for clarity). Selected bond lengths and angles: Cu(1)–N(9) = 1.994(3) Å, Cu(1)–N(3) = 2.007(3) Å, Cu(1)–N(12) = 2.015(3) Å, Cu(1)–N(6) = 2.019(3) Å, N(9)–Cu(1)–N(3) = 177.45(12)°, N(9)–Cu(1)–N(12) = 86.46(11)°, N(3)–Cu(1)–N(12) = 95.68(11)°, N(9)–Cu(1)–N(6) = 92.43(11)°, N(3)–Cu(1)–N(6) = 85.38(11)°, N(12)–Cu(1)–N(6) = 177.17(11)°.

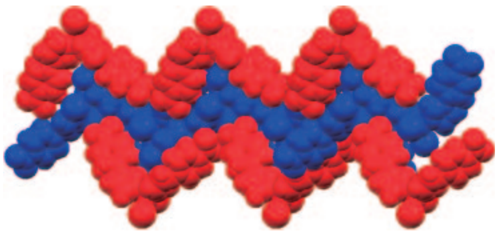


Figure 4. Zig-zag motif in **9** via O···H weak interaction and $\pi\cdots\pi$ stacking interaction.

zinc center are occupied by imidazolyl nitrogen of nopi, while other two by chloro groups. The angles about the metal center are comparable to those in tetrahedral systems with small deviations. One of the major differences between [Zn(cpi)$_2$Cl$_2$] and [Zn(nopi)$_2$Cl$_2$] lies in the absence of a 2-fold symmetry axis in [Zn(nopi)$_2$Cl$_2$]. The Zn–N and Zn–Cl bond distances [Zn(1)–N(1) = 2.031(2) Å, Zn(1)–N(4) = 2.020(2) Å, Zn(1)–Cl(1) = 2.2166(10) Å, and Zn(1)–Cl(2) = 2.2117(10) Å] are consistent with the values reported in the literature.[7b] The nitrophenyl ring is twisted with respect to the imidazole ring. Dihedral angles between the phenyl and imidazole ring planes are −32.7(4) and −28.6(4)°, respectively. Geometry about the nitrogen of –NO$_2$ groups is trigonal planer with sp^2 hybridization. The N–O bond distances differ slightly among themselves (N(3)–O(2) = 1.220(4) Å, N(3)–O(1) = 1.209(4) Å and N(6)–O(3) = 1.211(4) Å, N(6)–O(4) = 1.219(4) Å) and lie within the range for N–O single and N=O double bonds, indicating resonance in the –NO$_2$ group. The nitro group deviated a little from the plane of the phenyl ring suggesting extended conjugation with the phenyl ring.

The second category of the complexes are represented by formulations [M(nopi)$_6$](X)$_2$ (X = NO$_3^-$ and ClO$_4^-$). Due to the poor quality of the crystals, attempts to verify the structure of this type of complexes by single-crystal X-ray diffraction analyses were unsuccessful in our hands, however, spectral and analytical data corroborated well to proposed formulations. Reaction between the nopi and Cu(NO$_3$)$_2$•3H$_2$O afforded complex [Cu(nopi)$_4$(NO$_3$)$_2$] (**7**) possessing square-planner arrangement of nopi ligands about the metal center, unlike its cpi analog (Figure 3).[7a] In this complex four nopi ligands coordinated with the metal center along equatorial positions, while axial positions are occupied by weakly interacting nitrate ions leading to an overall *pseudo-octahedral* geometry. The Cu–N bond distances are consistent with coordination of the ligands with the metal center.[7a] The Cu–O distances are greater than the sum of covalent radii of Cu and O (Cu(1)–O(1) = 2.463 Å, Cu(1)–O(4) = 2.577 Å), suggesting absence of a covalent bond between them. Analogous to cpi and other nopi complexes, the ligand is not completely planar. Torsion angles between the plane of phenyl and imidazole rings are between 26.69 to 34.70°, while –NO$_2$ groups deviated from the phenyl ring plane from 3.05 to 13.65°.

Weak Interaction Studies. Crystal structures of **9** and **7** revealed the presence of extensive intra- and intermolecular C–H···X (X = O, N, and Cl) and $\pi\cdots\pi$ interactions which play a significant role in the building of supramolecular moieties.[4e,14] Interesting zig-zag motifs resulting from C–H···O and $\pi\cdots\pi$ are shown in Figure 4. Weak bonding interactions between oxygen of –NO$_2$ and C6 hydrogen in **9** leads to a unique zig-zag chain along crystallographic *a* axis (Figure 4). Centre to center separation of the phenyl rings from two different molecules are 3.648 Å (Figure S1), suggesting strong $\pi\cdots\pi$ stacking interactions between these molecules. The stacking is stabilized by zig-zag arrangement of these molecules.

Similarly in **7**, intermolecular π–π stacking interactions resulted in the creation of huge coordination networks from discrete molecules (Figures 5 and S2).[4e,14] Intermolecular face-to-face π–π interactions between discrete [Cu(nopi)$_4$]$^{2+}$ moieties involving nitrophenyl rings leads to a ladder motif shown in Figures 5 and S3. In addition, C–H···N interaction also leads to formation of an interesting structural motif (Figure S4).

Emission Study. The photoluminescence properties of complexes **1**–**6** were followed in DMSO at room temperature.

Measurements were carried out under analogous conditions. Upon excitation at their MLCT or d–d transition bands these do not exhibit any significant luminescence, while upon excitation at their intra-ligand transitions these exhibit moderate luminescence. Resulting data are summarized in the experimental section and comparative spectra of **1**–**6** are depicted in Figure 6. Interestingly, all the complexes upon excitation at 260–296 nm exhibited luminescence with emission maxima centered at 380–400 nm. It is analogous to that observed in the ligand nopi (emission maximum at 438 nm upon excitation at 284 nm). The emissions observed in these complexes have been tentatively assigned to the $\pi \rightarrow \pi^*$ intra-ligand fluorescence due to their close similarity with the emission bands in nopi.[7c]

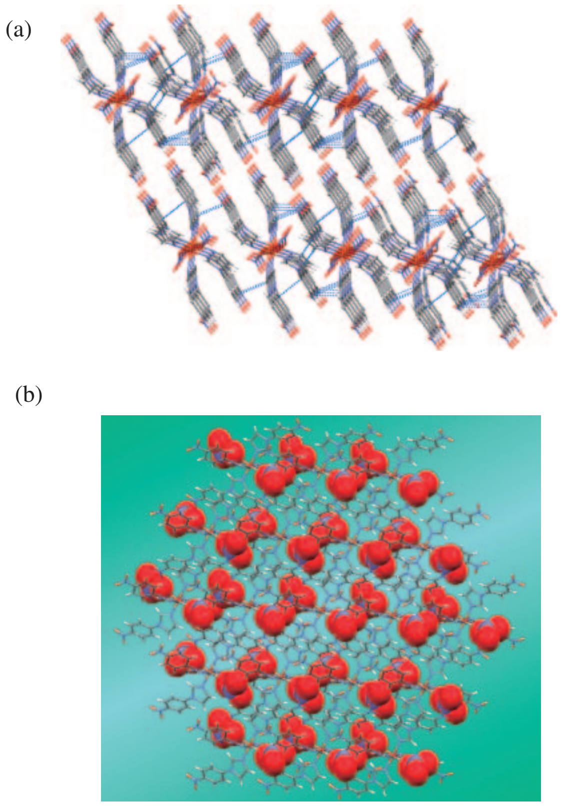


Figure 5. π–π stacking interaction in complex **7** (a) along crystallographic *a* axis and (b) along crystallographic *c* axis.

Pressed Pellet Conductivity Measurement. The electrical conductivity measurements on **1**–**8** pellets were made by conventional two probe technique in the temperature range 313–373 K. Figure 7 shows that the ln σ of the complexes **2**, **6**, and **7** decreases continuously with $1/T$, indicating that the complexes show typical semiconducting behavior over the entire temperature range. This plot is almost linear. The band gaps evaluated from these plots were 1.551 eV for **2**, 0.543 eV for **6**, 0.676 eV for **7** and these compounds exhibit very weakly conducting σ_{rt} in the range of rt 10^{-9}–10^{-5} S cm^{-1}.

Conclusion

Through this work we have described synthesis and characterization of novel monometallic complexes based on nopi and different 3d metal ions. All the complexes have been characterized by elemental analyses and spectral studies. Structure of $[\mathrm{Cu(nopi)_4(NO_3)_2}]$ (**7**) and $[\mathrm{Zn(nopi)_2Cl_2}]$ (**9**) have been determined by single-crystal X-ray diffraction analyses. Solid-state electrical conductance studies suggested that the cobalt complex **2** and copper complexes **6** and **7** exhibit good semiconducting behavior at room temperature. In addition, these complexes show moderate emissions at room temperature.

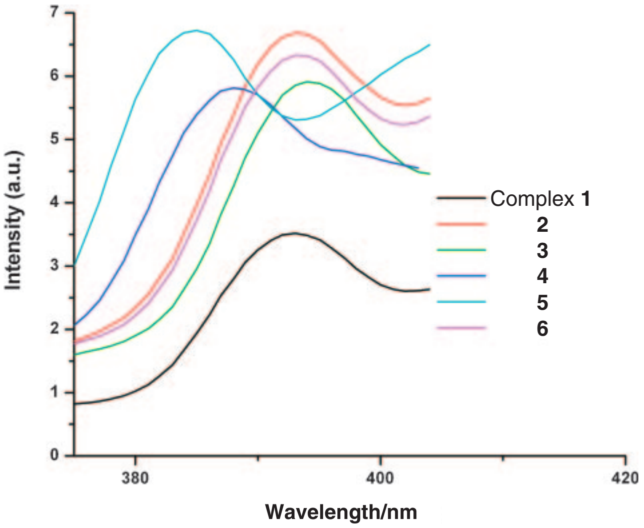


Figure 6. Emission spectra of complexes **1**–**6**.

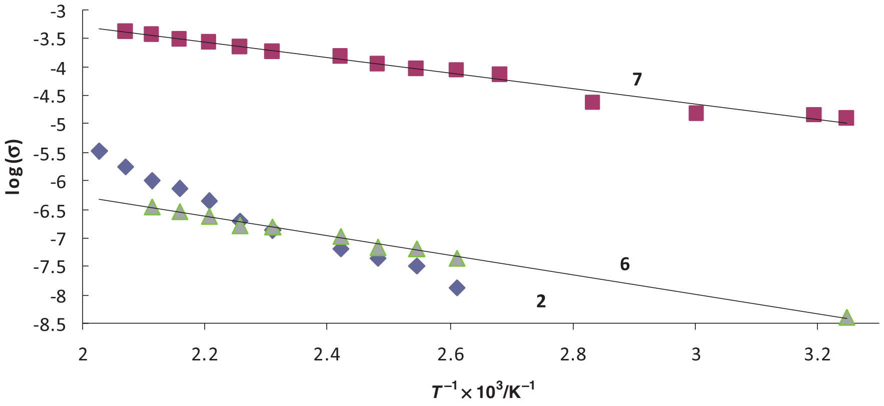


Figure 7. Temperature dependence of electrical conductivities of the complexes: rectangular bar **2**, cubic bar **6**, triangular bar **7**.

Thanks are due to the Department of Science and Technology, New Delhi, India for providing financial assistance SR/S1/IC-15/2006. A.K.S. acknowledges CSIR for awarding JRF 09/013(0127)/2007, EMR-I. The authors are also grateful to the Head Department of Chemistry, Faculty of Science, Banaras Hindu University, Varanasi (U.P.), India for extending facilities. Special thanks are due to Prof. Pradeep Mathur, In-charge, National Single Crystal X-ray Diffraction Facility, Indian Institute of Technology, Mumbai for providing single-crystal X-ray data.

Supporting Information

Structural motifs resulting from C–H···N and π–π stacking interactions and matrices for weak bonding interactions in **7** and **9** are gathered in supporting materials. Supplementary data associated with this article can be found free of cost. This material is available free of charge on the web at http://www.csj.jp/journals/bcsj/.

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