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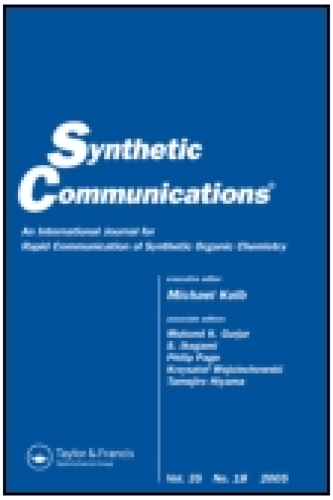

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Synthesis of Novel Schiff's Bases Containing Pyridine Rings

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Synthesis of Novel Schiff's Bases Containing Pyridine Rings

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ABSTRACT

Synthesis and characterization of six new Schiff's bases, potential hexadentate ligands, containing amide groups and pyridine rings with shallow structures are described. The two step reactions involving ring opening of isatoic anhydride with diamines followed by condensation with pyridine aldehydes proceed smoothly to give Schiff's bases containing pyridine rings in high purity and better yields.

Key Words: Schiff's bases; Amide group; Pyridine rings; Proteins.

INTRODUCTION

We have been attempting to develop new chelators, both open and closed (ring), with shallow structures.[1–3] The richest sources of concave surfaces

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are found in the binding and active sites of proteins and nucleic acids. The amide group is an important functional group of biomolecules and also yields useful information. The comparisons of the energies of the rotational barrier to amide rotation provides a means of characterization.[4] In view of the interest in the amide group [$R_2N{-}C{=}O$] in the coordination chemistry and biochemistry we have developed a series of new compounds containing $O{=}C{-}NR_2$ group along with $-NH_2$, $-COOH$, and $-OH$ groups[1–3] that can bind metal ions in a better way. Further, we have recently reported the non-template synthesis of di- and tetra-amide macrocyclic ligands using the diamine diamide compounds.[5] We have also investigated the catalytic applications of the *4f*-metal complexes of these ligands in organic synthesis.[6–8] The structures of the complexes were reported as shown in Fig. 1.

The ligands and their complexes, we have reported earlier deal with the orientation of the donor molecules to coordinate to the metal ions more effectively. In view of the interest and importance of polydentate ligands in developing macrocyclic ligands and supramolecular interactions between metal cations and also anions we have attempted to develop new polydentate ligands with donor groups, $O{=}C{-}NH$, $-NH_2$, $>C{=}N-$, and pyridine rings with probable shallow structures.

Isatoic anhydride **1** reacts with diamines **2**, **3**, or **4** at room temperature in water with the ring opening to form compounds, 2-amino-*N*-{2-[(2-aminobenzoyl)amino]-ethyl (**5**)/propyl (**6**)/phenyl (**7**)-benzamides, respectively.[1–3] The course of the reaction can be monitored with the expulsion of CO_2 with effervescence.

Condensation of compounds **5**, **6**, and **7** with 2-aminonicotinaldehyde **8** or pyridine-2-carbaldehyde **9** in the presence of *p*-toluene sulfonic acid (PTSA) in DMF resulted in the products **10–15** (Sch. 1) in the yields ranging between 65% and 85%.

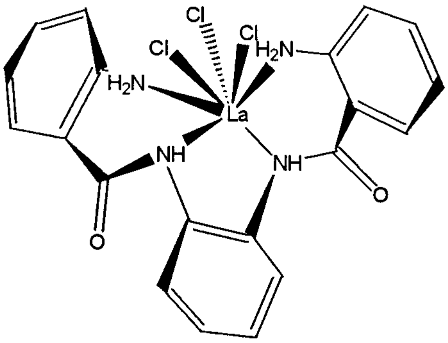

Figure 1. The structures of the complexes.

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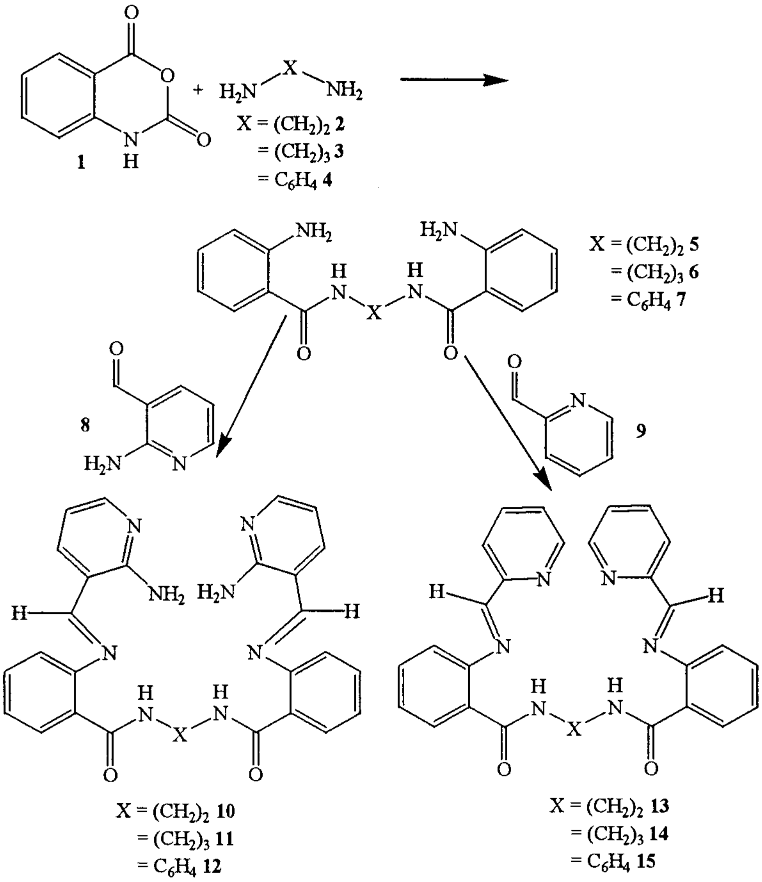
The compounds exhibit characteristic IR absorptions of the groups, amine $\nu(-NH_2)$, amide [$\nu(>C{=}O)$ and $\nu(C-N) + \delta(N-H)$], and $\nu(C{=}N)$. The ^1H NMR spectral absorptions of all the compounds recorded in DMSO-d_6 indicate unequivocally the formation of the title compounds. The mass spectra of the compounds exhibit the molecular ion peak and other fragments confirm the proposed formulas of the compounds. These compounds with an open structure tend to orient to develop a concave surface for coordination to metal ions. These compounds are found to modify the spectral and redox properties of transition metal ions.[9] We have carried out ring closure reactions on diamine compounds **5**, **6**, and **7** to obtain N_4-tetraazamacrocycles.[5]



Scheme 1.

The development of the compounds **10–15** is interesting as the search for supramolecular interactions[10–12] between the solid complex species and covalent molecules[13,14] and/or counter ions both in solid state and solution[15] is the field of current importance.

EXPERIMENTAL SECTION

Isatoic anhydride and pyridine-2-carbaldehyde were obtained from Aldrich Chemical Company, USA and used as received. 2-Aminonicotinaldehyde was prepared as described elsewhere.[16] All the solvents were distilled and stored over molecular sieves. Melting points (uncorrected) were determined in open capillary tubes using Cintex apparatus. Purity of the compounds was checked by TLC using Merk 60F-254 silica gel plates. The micro analysis was performed using Perkin Elmer Series II CHNS analyzer-2400. IR spectra in KBr discs were recorded using a Perkin Elmer-BX series FT-IR spectrophotometer. ^{1}H NMR spectra were recorded on Bruker ARX200 spectrometer. Mass spectrum was recorded using Varian MAT 311 A/AMD mass spectrometer. The electronic spectra in methanol were recorded on Shimadzu 2401 PC spectrometer.

2-Amino-*N*-{2-[(2-aminobenzoyl)amino] ethyl (5)/propyl (6)/phenyl (7)-benzamide. To a solution of 0.1 mol of the diamine (1,2-diaminoethane **2**, 6 g; 1,3-diaminopropane **3**, 7.4 g; or 1,2-diaminobenzene **4**, 10.8 g) in hot water and 0.2 mol (29.8 g) of powdered isatoic anhydride was added and stirred for 3 hr. Heating on water bath was continued till the effervescence of CO_2 gas ceased. The reaction mixture was allowed to stand over night and the product recrystallized from dioxane **5** or methanol **6** and **7.**

5. (23.2 g, 85%), m.p. 241°C. IR (KBr): 3460, 3360, 3275, 1620, 1550 cm^{-1}. ^{1}H NMR (DMSO-d_6) δ: 8.2_{br}, (2H, –CO–N*H*), $7.0–7.6_m$ (8H, Ar*H*'s), 4.3–4.7 (4H, –NH–C*H*$_2$–), 2.9 (4H, –N*H*$_2$). EIMS m/z: 298 (M^+). Anal. calcd for $C_{16}H_{18}N_4O_2$: C, 64.41; H, 6.08; N, 18.78. Found: C, 64.22; H, 5.94; N, 18.71.

6. (24.8 g, 87%), m.p. 168°C, IR (KBr): 3460, 3360, 3275, 1665, 1615, 1535 cm^{-1}. ^{1}H NMR (DMSO-d_6) δ: 8.3_t (2H, –CO–N*H*–), 6.6–7.9 (8H, Ar*H*'s), 4.5_{br} (4H, –N*H*$_2$), 3.3_m (4H, –HN–C*H*$_2$–), 1.55_m (2H, –C*H*$_2$–). EIMS m/z: 312 (M^+). Anal. calcd for $C_{17}H_{20}N_4O_2$: C, 65.37; H, 6.45; N, 17.94. Found: C, 65.13; H, 6.28; N, 17.81.

7. (28.5 g, 90%), m.p. 218°C, IR (KBr): 3450, 3360, 1620, 1500 cm^{-1}, ^{1}H NMR (DMSO-d^6) δ: 8.5 (2H, –CO–N*H*–), $7.2–7.7_m$ (12H, Ar*H*'s), 3.15_{br} (4H, –N*H*$_2$). EIMS m/z: 346 (M^+). Anal. calcd for $C_{20}H_{18}N_4O_2$: C, 69.35; H, 5.24; N, 16.17. Found: C, 68.87; H, 5.08; N, 15.85.

***N*,*N*′-*bis*-2-{(2-amino-pyridine-3-ylmethylene)amino benzoyl)}-1,2-diaminoethane (8), 1,3-diaminopropane (11), and 1,2-diaminobenzene (12).** A solution of 0.03 mol each of **5** (7.67 g), **6** (8.52 g), or **7** (9.54 g) and 0.06 mol (6.5 g) of *o*-aminonicotinaldehyde **8** and PTSA (0.1 g) dissolved in 120 mL of DMF was refluxed for 5 hr, cooled and poured over crushed ice. The solid was filtered and recrystallized from methanol.

10. (8.4 g, 66%), m.p. 170°C, IR (KBr): 3325, 1617, 1520, 1450 cm^{-1}. UV—347, 304, 217 nm. ^1H NMR (DMSO-d_6) δ: 9.85, (2H, $-CO-NH-$), 6.6–8.3 (16H, Ar*H*'s, and $-N{=}CH-$), 4.74$_{br}$ (4H, $-NH_2$), 3.7$_m$ (4H, $-CH_2-CH_2-$). EIMS m/z: 506.1 (M^+), 402, 298, 239, 162, 120 (100%), 92, 78, 65. Anal. calcd for $C_{28}H_{26}N_8O_2$: C, 66.39; H, 5.17; N, 22.12. Found: C, 65.98; H, 5.74; N, 21.75.

11. (10.8 g, 73%), m.p. 110°C, IR (KBr): 3337, 1616, 1525, 1450 cm^{-1}. UV—307, 232 nm. ^1H NMR (DMSO-d_6) δ: 9.45$_s$ (2H, $-CO-NH-$), 6.66–8.16$_m$ (20H, Ar*H*'s, and $-N{=}CH-$), 4.74$_{br}$ (4H, $-NH_2$), 3.52$_m$ (4H, HN–CH_2-), 1.79$_m$ (2H, $-CH_2-$). EIMS m/z: 520 (M^+), 416, 312, 239, 173, 137, 120 (100%), 92, 65. Anal. calcd for $C_{29}H_{28}N_8O_2$: C, 66.91; H, 5.42; N, 21.52. Found: C, 66.38; H, 5.14; N, 21.15.

12. (12.5 g, 82%), m.p. 120°C, IR (KBr): 3354, 1670, 1612, 1500, 1450 cm^{-1}. UV—340, 301, 220, 206 nm. ^1H NMR (DMSO-d_6) δ: 9.86$_s$ ($-CO-NH-$), 6.66–8.16$_m$ (20H, Ar*H*'s, and $-N{=}CH-$), 4.52$_{br}$ (4H, $-NH_2$). EIMS m/z: 554 (M^+), 539, 450, 356, 328, 209, 120 (100%), 92, 65. Anal. calcd for $C_{32}H_{26}N_8O_2$: C, 69.30; H, 4.73; N, 20.20. Found: C, 68.88; H, 4.54; N, 20.43.

***N*,*N*′-bis-2-{(pyridine-2-ylmethylene) amino-bezoyl}-1,2-diaminoethane (13), 1,3-diaminopropane (14), and 1,2-diaminobenzene (15).** A 0.03 mol each of **5** (7.67 g), **6** (8.52 g), or **7** (9.54 g) was dissolved in 100 mL DMF. To this 30-mL DMF solution of pyridine-2-carbaldehyde **9** (0.06 mol, 6.4 g) was added separately. The mixture was refluxed for 5 hr in presence of 0.1 g PTSA. Then, it was cooled and poured over crushed ice and stirred over night. The products were filtered and washed with water and cold methanol. Recrystallization from methanol in presence of activated charcoal yielded TLC pure products.

13. (8.3 g, 65%), m.p. 120°C, IR (KBr): 3329, 1636, 1508, 1456 cm^{-1}. UV—331, 247, 239 nm. ^1H NMR (DMSO-d_6) δ: 8.667$_t$ (2H, $-CO-NH-$), 6.78–8.35 (18H, Ar*H*'s, and $-N{=}CH$), 3.55 (4H, $-HN-CH_2$). EIMS m/z: 476.5 (M^+), 387.4. 298.3, 224.2, 163.2, 150.2, 137.1, 120.2 (100%), 92.1, 78.1, 65.1, 39.1. Anal. calcd for $C_{28}H_{24}N_6O_2$: C, 70.57; H, 5.08; N, 17.64. Found: C, 69.97; H, 5.17; N, 17.52.

14. (10.0 g, 72%), m.p. 90°C, IR (KBr): 3341, 1636, 1512, 1466 cm^{-1}. UV—330, 235 nm. ^1H NMR (DMSO-d_6) δ: 8.55$_t$ (2H, $-OC-NH-$), 6.52–7.89$_m$ (18H, Ar*H*'s, and $-N{=}CH-$), 3.50$_{br}$ (4H, $-HN-CH_2-$), 1.85$_{qu}$ (2H, $-CH_2-$). EIMS m/z: 490 (M^+), 401, 312, 224, 163, 150, 137, 120

(100%), 92, 65. Anal. calcd for $C_{29}H_{26}N_6O_2$: C, 71.00; H, 5.34; N, 17.13. Found: C, 69.65; H, 5.51; N, 16.56.

15. (12.1 g, 81%), m.p. 98°C, IR (KBr) 3432, 1636, 1499, 1450 cm^{-1}. UV—341, 249, 225 nm. ^1H NMR (DMSO-d_6) δ: 9.87 (2H, $-OC-NH-$), 6.68–8.61 (22H, Ar*H*'s, and $-N{=}CH-$). EIMS m/z: 524 (M^+), 435, 346, 209, 181, 120 (100%), 92, 78, 65. Anal. calcd for $C_{32}H_{24}N_6O_2$: C, 73.27; H, 4.61; N, 16.02. Found: C, 72.86; H, 4.88; N, 15.83.

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