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Silica-Supported Perchloric Acid ($HClO_4/SiO_2$) as Efficient Catalyst for the Synthesis of Tetraazamacrocyclic Complexes of Transition Metals[1]

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Abstract—Silica-supported perchloric acid ($HClO_4/SiO_2$) was used to catalyze the synthesis of tetraazamacrocyclic complexes of Co(II), Ni(II), Cu(II), and Zn(II) from the corresponding metal chlorides, nitrates, or acetates, isatin, and benzene-1,2-diamine in ethanol. The use of $HClO_4/SiO_2$ as catalyst allowed the reaction to be performed under stirring at room temperature instead of traditional reflux and completed in two hours. The synthesized complexes were characterized by molar conductance and magnetic susceptibility measurements, IR, electronic, ^{1}H NMR, and mass spectra, and thermogravimetric and X-ray powder analyses. On the basis of these data, six-coordinate octahedral geometry was proposed for all complexes. The synthesized complexes were also tested for antimicrobial activity.

Keywords: isatin, benzene-1,2-diamine, octahedral coordination, magnetic susceptibility, antimicrobial activity

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Syntheses of macrocyclic complexes generally include refluxing solutions of ligands and metal salts for an appropriate time. In template methods, the complex forming components react with each other in the presence of metal ions [1–5]. Thus template method is important in cases where ligand isolation is not possible. Syntheses of macrocyclic complexes using condensation catalysts such as DMAP and DCC have been reported [6, 7]. The use of solid supported catalyst for the synthesis of complexes is also known [8], but till date this area of research seems to be little explored. This has prompted us to undertake study of synthesis of macrocyclic complexes using solid supported catalysts.

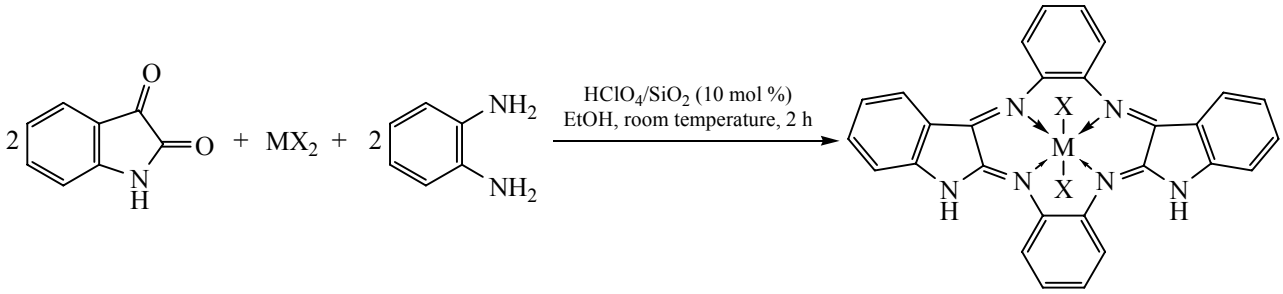
Herein we report the use of silica-supported perchloric acid ($HClO_4/SiO_2$) as catalyst for the synthesis of tetraazamacrocyclic complexes of transition metal ions, such as Co(II), Ni(II), Cu(II), and Zn(II), from isatin, benzene-1,2-diamine, and the corresponding metal chlorides, nitrates, and acetates in ethanolic medium. The complexes were synthesized by simply stirring the complex forming components at room temperature (Scheme 1) and were characterized by molar conductance and magnetic susceptibility measurements and IR and electronic spectra. In addition, ^{1}H NMR and mass spectra and thermogravimetric (TGA) and X-ray powder diffraction data were obtained for some complexes. On the basis of these results, a six-coordinate octahedral geometry was proposed for all complexes. The synthesized complexes were also screened for antimicrobial activity.

The conventional reflux method requires 8–10 h for the reaction completion [9–11], whereas the same reaction using silica-supported perchloric acid ($HClO_4/SiO_2$) as catalyst was complete within two hours at room temperature. Complexes **1**–**12** had the general compositions $[M(C_{28}H_{18}Cl_2N_6)]$ for chloride, $[M(C_{28}H_{18}N_8O_6)]$ for nitrate, and $[M(C_{32}H_{24}CoN_6O_4)]$ for acetate complexes. All complexes **1**–**12** were thermally stable (decomposition point >250°C) and colored (Table 1). They were partially soluble in methanol, water, and ethanol, readily soluble in DMSO and DMF, and insoluble in chloroform, methylene chloride, ethyl acetate, and acetone.

The IR spectra of complexes **1**–**12** (Table 1) lacked absorption bands typical of free amino groups of benzene-1,2-diamine (two bands at 3210–3435 cm^{-1})

[1] The text was submitted by the authors in English.

Scheme 1.



1–12

1–4, X = Cl; **5–8**, X = NO_3; **9–12**, X = AcO; **1**, **5**, **9**, M = Co(II); **2**, **6**, **10**, M = Ni(II); **3**, **7**, **11**, M = Cu(II); **4**, **8**, **12**, M = Zn(II).

and carbonyl stretching modes of isatin (1700 cm^{-1}), which indicated condensation of the carbonyl group of isatin with amino groups of benzene-1,2-diamine [12, 13]. Instead, a single medium-intensity band at 3265–3320 cm^{-1} was observed, which may be assigned to stretching vibrations of the N–H group of the isatin moiety [14]. Another absorption band in the region 1606–1644 cm^{-1} may be assigned to C=N stretching vibrations [15, 16]. These findings provide a strong evidence for the formation of macrocyclic skeleton [17]. Reduction of the n(C=N) frequency may be accounted for by the drift of lone pair electron density on the azomethine nitrogen toward the central metal atom [10, 14, 18]. Band observed in the region 1015–1355 cm^{-1} may be due to C–N stretching vibrations [19]. Medium-intensity bands in the region 1500–1580 cm^{-1} were attributed to stretching vibrations of aromatic C=C bonds in the benzene fragments. The M–N stretching bands were observed in the range 421–490 cm^{-1}, which confirmed coordination of the azomethine nitrogen atoms to the central metal ion [10, 20]. Peaks corresponding to the coordinated nitrate and acetate groups were present in the ranges 1300–1500 cm^{-1} and 1000–1350 cm^{-1}, respectively, indicating unidentate coordination of these ligands to the metal [21, 22].

Table 1. Molecular weights, yields, colors, decomposition points, and IR spectral data of macrocyclic complexes **1–12**

Comp. no.	Formula	Molecular weight	Yield, %	Color	Decomp. point, °C	IR spectrum (KBr), ν, cm^{-1}			
						N–H	C=N	C=C	M–N
1	$C_{28}H_{18}Cl_2CoN_6$	567	63	Red	>250	3247	1642	1530	433
2	$C_{28}H_{18}Cl_2NiN_6$	566	68	Light green	>250	3210	1644	1504	473
3	$C_{28}H_{18}Cl_2CuN_6$	571	70	Green	>250	3200	1630	1528	450
4	$C_{28}H_{18}Cl_2ZnN_6$	572	66	Light brown	>250	3240	1633	1555	434
5	$C_{28}H_{18}CoN_8O_6$	621	64	Light red	>250	3320	1662	1544	472
6	$C_{28}H_{18}NiN_8O_6$	620	60	Faint green	>250	3200	1612	1580	457
7	$C_{28}H_{18}CuN_8O_6$	625	72	Green	>250	3200	1606	1520	460
8	$C_{28}H_{18}ZnN_8O_6$	626	68	Faint yellow	>250	3230	1614	1547	455
9	$C_{32}H_{24}CoN_6O_4$	615	61	Light red	>250	3290	1635	1550	424
10	$C_{32}H_{24}NiN_6O_4$	614	67	Faint green	>250	3220	1606	1540	457
11	$C_{32}H_{24}CuN_6O_4$	619	71	Green	>250	3235	1614	1549	440
12	$C_{32}H_{24}ZnN_6O_4$	620	60	Light brown	>250	3200	1615	1504	469

Table 2. Electronic spectral data, molar conductances, and magnetic moments of complexes **1**–**12**

Compound no.	λ_{max}, nm	Assignment	Molar conductance, Ω^{-1} cm^2 mol^{-1}	Magnetic moment μ_{eff}, B.M.
1	710 520	$^4T_{1g}\rightarrow{}^4A_{2g}$ (F) $^4T_{1g}\rightarrow{}^4T_{1g}$ (P)	18	4.90
2	610 350 972 860	$^3A_{2g}\rightarrow{}^3T_{1g}$ (F) $^3A_{2g}\rightarrow{}^3T_{1g}$ (P) $^3B_{1g}\rightarrow{}^3E_g$ $^3B_{1g}\rightarrow{}^3B_{2g}$	15	2.92
3	680 540	$^2B_{1g}\rightarrow{}^2E_g$ $^2B_{1g}\rightarrow{}^2B_{2g}$	11	1.73
4	530	LMCT	10	Diamagnetic
5	780 510	$^4T_{1g}\rightarrow{}^4A_{2g}$ (F) $^4T_{1g}\rightarrow{}^4T_{1g}$ (P)	14	4.92
6	600 360	$^3A_{2g}\rightarrow{}^3T_{1g}$ (F) $^3A_{2g}\rightarrow{}^3T_{1g}$ (P)	19	2.90
7	685 520	$^2B_{1g}\rightarrow{}^2E_g$ $^2B_{1g}\rightarrow{}^2B_{2g}$	22	1.77
8	540	LMCT	15	Diamagnetic
9	790 530	$^4T_{1g}\rightarrow{}^4A_{2g}$ (F) $^4T_{1g}\rightarrow{}^4T_{1g}$ (P)	18	4.96
10	600 355	$^3A_{2g}\rightarrow{}^3T_{1g}$ (F) $^3A_{2g}\rightarrow{}^3T_{1g}$ (P)	13	2.98
11	650 540	$^2B_{1g}\rightarrow{}^2E_g$ $^2B_{1g}\rightarrow{}^2B_{2g}$	17	1.83
12	520	LMCT	19	Diamagnetic

The electronic absorption spectra of the Co(II) complexes in DMSO solution displayed bands with their maxima at λ 710–790 and 500–530 nm due to $^4T_{1g}\rightarrow{}^4T_{2g}$ (F) and $^4T_{1g}\rightarrow{}^4T_{1g}$ (P) electronic transitions (Table 2). These data support octahedral geometry of cobalt complexes **1**, **5**, and **9** [23, 24]. Nickel(II) complex **2** showed four bands in the electronic spectrum, two of which (λ 600–580 and 350–359 nm) were assigned to $^3A_{2g}\rightarrow{}^3T_{1g}$ (F) and $^3A_{2g}\rightarrow{}^3T_{1g}$ (P) transitions, respectively. The remaining two bands observed in the regions λ 1030–970 and 851–814 nm correspond to $^3B_{1g}\rightarrow{}^3E_g$ and $^3B_{1g}\rightarrow{}^3B_{2g}$ transitions. Analogous $^3A_{2g}\rightarrow{}^3T_{1g}$ (F) and $^3A_{2g}\rightarrow{}^3T_{1g}$ (P) bands were observed in the spectra of Ni(II) complexes **6** and **10**, indicating distorted octahedral geometry of the Ni(II) complexes [10, 25]. The electronic spectra of Cu(II) complexes contained two low-energy bands in the regions λ 510–565 and 612–687 nm due to $^2B_{1g}\rightarrow{}^2E_g$ and $^2B_{1g}\rightarrow{}^2B_{2g}$ transitions. These data are consistent with octahedral geometry of Cu(II) complexes **3**, **7**, and **11** [10, 25]. The absorption band at λ = 380–440 nm in the spectra of Zn(II) complexes **4**, **8**, and **12** was assigned to the ligand→metal charge transfer (LMCT) as an indication of octahedral geometry [26].

The magnetic moments for all the synthesized complexes were measured at room temperature using copper(II) sulfate as reference (Table 2). The magnetic moments of Co(II) complexes **1**, **5**, and **9** ranged from 4.90 to 4.96 B.M., which corresponded to three unpaired electrons [25]. The magnetic moments of Ni(II) complexes **2**, **6**, and **10** were in the range 2.90–2.98 B.M., indicating the presence of two unpaired electrons [25], and the magnetic moments of Cu(II) complexes **3**, **7**, and **11** were estimated at 1.73–1.83 B.M. (one unpaired electron) [25]. Zinc(II) complexes **4**, **8**, and **12** were diamagnetic, in keeping with the d^{10} configuration of Zn therein [27].

Table 3. TGA data for Cu(II) complex **3**

Temperature range, °C	Weight loss, %		Decomposition product
	observed	calculated	
30–110	5.357	5.357	Lattice water
110–310	5.304	5.304	Coordinated chloride ion
320–380	20.90	20.89	Organic ligand
400–500	58.19	58.20	Copper residue

The molar conductances of macrocyclic complexes **1**–**12** were measured for 10^{-3} M solutions in DMSO. The observed molar conductance values (10–22 Ω^{-1} cm^{-2} mol^{-1}) indicated that complexes **1**–**12** are nonelectrolytes [28, 29].

The ^{1}H NMR spectrum of Zinc(II) chloride complex **4** contained two signals, a singlet at δ = 12.00 ppm due to NH proton of the isatin fragment [30] and a multiplet in the region δ = 7.20–7.90 ppm due to aromatic protons in the isatin and diaminobenzene moieties [31, 32]. Copper(II) acetate complex **11** showed the molecular ion peak with *m*/*z* 618 $[M - 1]^+$, which was consistent with the molecular weight calculated for the proposed structure.

We also performed thermogravimetric analysis (TGA) of copper(II) chloride complex **3** (Table 3). The TGA curve was recorded in the temperature range from 10 to 500°C. The first decomposition step (30–110°C) with a weight loss of 5.357% (calculated 5.357%) may be attributed to elimination of lattice water [33, 34]. The second step (110–310°C) was characterized by a weight loss of 5.304% (calcd. 5.304%) due to elimination of coordinated chlorine atoms. The organic ligand decomposed in the range 320–380°C with a weight loss of 20.90% (calculated 20.89%), and the last step of decomposition was observed in the range 400–500°C (decomposition of copper final residue) [34–36].

The X-ray powder diffraction study was performed for Cu(II) chloride complex **3** as an example. The X-ray powder pattern was obtained in the θ range 5°–70° at λ = 1.54060 Å. The diffractogram and associated data depicted 2θ values for each peak, relative intensity, and inter-planar spacings (*d* values). The major peaks (with relative intensities greater than 10%) have been indexed using a computer program. The indexing method also afforded the Miller indices (*h k l*), unit cell parameter, and unit cell volume. The lattice constant values are as follows: *a* = 21.620 Å, *b* = 1 Å, *c* 3.8210 Å. In keeping with these cell parameters, the conditions $a \neq b \neq c$ and α = β = γ are met for the sample to be orthorhombic system [8, 34, 37].

Table 4. Antibacterial and antifungal activities of complexes **1**–**12** and some standard drugs (*c* = 1.0 mg/mL)

Comp. no.	Inhibition zone,[a] mm		
	B. subtilis MTCC-8979	*E. coli* MTTC- 443	*C. albicans* MTTC-227
1	14	11	18
2	07	–	–
3	08	12	07
4	27	12	17
5	15	13	14
6	13	–	08
7	10	13	10
8	20	10	11
9	16	12	20
10	09	12	09
11	10	11	11
12	15	–	–
Streptomycin	30	31	–
Amphotericin B	–	–	29
DMSO (control)	–	–	–

[a] Activity ranges: significant (15–28 mm), medium (8–14 mm), no activity (–).

Metal complexes **1**–**12** were screened for antibacterial activity against *B. subtilis* and *E. coli* and antifungal activity against *C. albicans* (Table 4). The inhibition zones produced by the synthesized macrocyclic complexes were measured and compared with those for standard antibiotic streptomycin and antifungal drug Amphotericin B. Cobalt(II) and zinc(II) complexes **4**, **5**, **8**, **9**, and **12** showed a significant antibacterial activity against *B. subtilis* (inhibition zone diameter 15–27 mm), while nickel(II) and copper(II) complexes were moderately active (7–13 mm). Significant antifungal activity against *C. albicans* was found for Co(II) and Zn(II) complexes **1**, **4**, and **9**, whereas copper(II) chloride and zinc(II) chloride, nitrate, and acetate complexes showed moderate activity. Dimethyl sulfoxide was used as control (no inhibition).

In summary, silica-supported perchloric acid ($HClO_4/SiO_2$) efficiently catalyzed the synthesis of Co(II), Ni(II), Cu(II), and Zn(II) complexes by template condensation of isatin with benznene-1,2-diamine in the presence of the corresponding transition metal chlorides, nitrates, and acetates. The resulting complexes were characterized by various spectral and analytical methods and were assigned octahedral geometry on the basis of these data.

EXPERIMENTAL

All chemicals used in the present study were of AR grade. Isatin and benzene-1,2-diamine were purchased from SD Fine-Chem Ltd., and transition metal salts were purchased from Spectrochem Pvt. Ltd. The solvents were distilled and dried over molecular sieves before use.

The molar conductances of complexes **1**–**12** were measured from 10^{-3} M solutions in DMSO at room temperature using an Equiptronics Model EQ-664 conductivity meter with a built-in magnetic stirrer. The magnetic susceptibilities were determined on an SES Instruments Model EMU-50 Gouy balance at room temperature using copper(II) sulfate as standard. The IR spectra (4000–400 cm^{-1}) were recorded in KBr pellets on a Perkin Elmer spectrometer GX. The electronic spectra were recorded in DMSO on a Shimadzu UV-1600 spectrophotometer. The ^1H NMR spectrum of **4** was measured on a Bruker Avance II 400 spectrometer using DMSO-d_6 (spectroscopic grade) as solvent and tetramethylsilane as reference. The mass spectrum of **11** (electrospray ionization) was recorded on a Bruker micrOTOF-Q instrument. Thermogravimetric and X-ray powder diffraction analyses of Cu(II) chloride complex **3** were performed using TA Instruments SDT-2960 (USA) and PANalytical X'Pert-Pro XRD, respectively.

Silica-supported perchloric acid. The catalyst was prepared according to the procedure reported previously [38, 39]. Silica gel (200–400 mesh), 23.7 g, was dispersed in 70 mL of diethyl ether, 1.8 g (12.5 mmol) of 70% aqueous perchloric acid was added, the mixture was concentrated, and the residue was heated for 72 h at 100°C under reduced pressure to obtain $HClO_4/SiO_2$ (0.5 mmol/g) as a free-flowing powder.

Macrocyclic complexes 1–12 *(general procedure).* Cobalt(II), nickel(II), copper(II), or zinc(II) chloride, nitrate, or acetate, 0.05 mol, was dissolved in 25 mL of ethanol in a round-bottom flask. Benzene-1,2-diamine, 0.10 mol, was added under continuous stirring, $HClO_4/SiO_2$ (10 mol %) was then added, and the mixture was stirred for 10 min. Isatin, 0.10 mol, was added, and the reaction mixture was stirred for 2 h at room temperature. The progress of the reaction was monitored by TLC ($CHCl_3$–MeOH, 9 : 1) every 30 min. When the reaction was complete, the colored solid was filtered off and washed with acetone and diethyl ether. The dry solid was dissolved in 10 mL of DMF or DMSO, the undissolved material (catalyst) was filtered off for recovery purpose, the filtrate was concentrated, and the residue was dried in air.

Antimicrobial activity. Complexes **1–12** were screened for antimicrobial activity against *Bacillus Subtilis* (MTCC-8979), *Escherichia coli* (MTCC-443), and *Candida albicans* (MTCC-227) by the disc diffusion method. The complexes were dissolved in DMSO and sterilized by filtering through a 0.45-μm Millipore filter. Nutrient agar (NA, antibacterial activity) and potato dextrose agar (PDA, antifungal activity) media were prepared and sterilized in an autoclave and transferred to preliminarily sterilized Petri dishes. After solidification, Petri dishes were inoculated with bacterial organisms in sterile nutrient agar medium at 45°C or fungal organisms in sterile potato dextrose agar medium at 45°C under aseptic conditions. Sterile Whatman filter paper discs were impregnated with a solution of complex **1–12** to a concentration of 1 mg/disc and were placed in the organism-impregnated Petri dishes under sterile condition. Standard antibiotic discs of streptomycin (100 μg/disc) and Amphotericin B (100 μg/disc) were used as positive control, while DMSO was used as negative control. The dishes were incubated for 24 h at 37 ± 1°C for antibacterial activity or for 48 h at 37 ± 1°C for antifungal activity. The zone of inhibition was calculated by measuring the minimum dimension of the zone with no microbial growth around the disc [40].

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