CHAPTER – II

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2.1 General Description

All the solvents and chemicals were purified and dried before use according to standard procedures [1,2]. Solvents were generally removed by distillation at reduced pressure or at atmospheric pressure and the liquid products were purified by fractional distillation at reduced pressure.

Boiling points (uncorrected) were those of middle fraction. Solid products were purified either by recrystallization from suitable solvents (whenever possible) or by washing with more than one solvents. Melting points recorded were uncorrected.

Purity of the compounds were checked by elemental analyses. Micro-analysis of C, H and N of the compounds were carried out on Elementar Vario EL III, Carlo Erba 1108 elemental analyzers at the Sophisticated Analytical Instrument Facility, Central Drug Research Institute, Lucknow, India. Elemental analyses of metals and halogen(s) were done in our laboratory by conventional methods after decomposing the compounds with concentrated mineral acids. Primarily elemental analyses of vanadium and nitrogen were also done in our laboratory by usual methods (vanadium as V_2O_5 and nitrogen by Duma's method).

Infrared spectra were recorded (in KBr disc or nujol mull or hexachlorobutadiene; more than one media were used for some compounds) on a Perkin-Elmer 1330 and L120-000A FTIR spectrophotometers in our laboratory.

Electronic spectra were also taken as nujol mull or in suitable solvents in our laboratory on a Hitachi 200-20 and Shimadzu UV-2401PC spectrophotometers. ^{1}H NMR spectra of the ligands and complexes were recorded with a Brüker (300 MHz) NMR obtained from Indian Institute of Chemical Biology, Kolkata–700032 and at the Sophisticated Analytical Instrument Facility, Central Drug Research Institute, Lucknow,

India. ESR spectra were also recorded on Varian, E-112 ESR spectrometer at the Sophisticated Analytical Instrument Facility, Bose Institute, Kolkata.

Magnetic susceptibilities were measured in a Gouy balance at room temperature. The Gouy tubes were calibrated using $Hg[Co(SCN)_4]$ [3] and the μ_{eff} values were calculated following Figgis and Lewis [4].

Conductance measurements were made with a conductivity bridge (Elico Pvt. Ltd., Model CM 80). Molecular weights were determined by Rast's method and by Osmometry with a Hitachi Perkin Elmer Model 115 Vapour Pressure Osmometer by using benzene or methylene chloride as solvent. The measurements were made within five minutes of preparation of the solution.

The thermal measurements were carried out by Perkin Elmer Pyris Diamond TG/DTA to determine the composition temperatures of the complexes and to determine in which heat range the electrical measurements can be made. The TG curves were recorded in the temperature range of 20-400 °C for 20 °C/min heating rate.

Experimental samples were prepared from the complexes in the form of tablets and their thickness was ~0.1 cm at a pressure of approximately $1x10^8$ Pascal. These tablets were placed between two copper electrodes with silver paste and contacts were tested to be ohmic. The electrical conductivities of the prepared complexes were measured with a Keithley 6514 system electrometer, by applying *dc* voltage using Keithley 230 programmable voltage source. The conductivities were calculated by using the general equation of $\sigma = (I/V_c)(d/a)$, where (I) is the current in ampere, V_c the potential drop across the sample of cross-sectional area (a) and thickness (d).

Optical absorption spectra were taken by using a UV-Vis. spectrophotometer (Perkin-Elmer Lambda 2S Double Beam), in the wavelength range 190-1100 nm.

Crystal data were collected on a Brüker-AXS APEX CCD diffractometer with monochromatized Mo-Kα radiation (λ = 0.71073 Å) The data-set was treated with SADABS absorption corrections based on redundant multiscan data [5]. Structure factors are contained in the SHELXTL6.12 programme library [5].

Powder X-ray diffraction (XRD) pattern, obtained using an X-ray powder diffractometer (Rigaku Geigerflex) with $CuK_{\alpha 1}$ (λ=1.54056 Å) source.

2.2 Preparation of the Starting Compounds / Salts

2.2.1 Preparation of 3-formylsalicylic acid, H_2fsa

3-Formylsalicylic acid was prepared according to Duff and Bills [6]. Yield 67 %, m p. 178-179 °C (lit. 178-180 °C).

Found: C, 57.88, H, 3.67 %

Calculated for $C_8H_6O_4$: C, 57.84, H, 3.64 %

2.2.2 Preparation of 1,2-di(*o*-aminophenylthio)ethane

The above compound was prepared according to the literature [7,8] published previously. Yield 85 %, m.p. 78 °C (lit. 77.5 °C).

Found: C, 60.91, H, 5.85, N, 10.19 %

Calculated for $C_{14}H_{16}N_2S_2$: C, 60.83, H, 5.83, N, 10.13 %

2.2.3 Preparation of morpholine N-thiohydrazide, Hmth

The compound was prepared according to the previously published method [9]. Yield 80 %, m.p. 177 °C (lit 178 °C).

Found: C, 37.35, H, 6.89, N, 26.16 %

Calculated for $C_5H_{11}N_3OS$: C, 37.26, H, 6.83, N, 26.08 %

2.2.4 Preparation of $Cr(CH_3COO)_3.6H_2O$

$Cr(CH_3COO)_3.6H_2O$ was prepared as described in the literature [10].

2.2.5 Preparation of $Mn(CH_3COO)_3.2H_2O$

$Mn(CH_3COO)_3.2H_2O$ was prepared as described in the literature [11].

2.2.6 Preparation of Na_2PdCl_4

The palladium(II) complex, Na_2PdCl_4 was prepared from $PdCl_2$ by the standard method published previously [12].

2.2.7 Preparation of Vanadium(IV)oxy(acetylacetonate), $[VO(acac)_2]$

$[VO(acac)_2]$ was prepared according to the method of Rowe *et al* [13].

2.2.8 Preparation of Vanadyl(IV)acetate, $[VO(CH_3COO)_2]$

$[VO(CH_3COO)_2]$ was prepared by a well known standard procedure [14].

2.2.9 Preparation of $(\pi\text{-}C_5H_5)_2Ti(OMe)Cl_2$, $(OMe)_2TiCl_2$ and $(\pi\text{-}C_5H_5)TiCl_3$

The compounds $(\pi\text{-}C_5H_5)_2Ti(OMe)Cl_2$, $(OMe)_2TiCl_2$ and $(\pi\text{-}C_5H_5)TiCl_3$ were prepared by early published literature methods [15-17].

2.2.10 Preparation of Me_2SnCl_2, Ph_2SnCl_2, $MeSnCl_3$ and $PhSnCl_3$

The tin compounds Me_2SnCl_2, Ph_2SnCl_2, $MeSnCl_3$ and $PhSnCl_3$ were prepared by the methods of Luijten and van der Kerk [18].

2.2.11 Preparation of $Me_3SiC{\equiv}CPh$

The compound $Me_3SiC{\equiv}CPh$ was prepared as described in literature [19,20].

2.2.12 Source of di(π-cyclopentadienyl)titanium(IV)dichloride, $(\pi\text{-}C_5H_5)_2TiCl_2$ and di(π-cyclopentadienyl)zirconium(IV) dichloride, $(\pi\text{-}C_5H_5)_2ZrCl_2$

Di(π-cyclopentadienyl)titanium(IV)dichloride, $(\pi\text{-}C_5H_5)_2TiCl_2$ and di(π-cyclopentadienyl)zirconium(IV) dichloride, $(\pi\text{-}C_5H_5)_2ZrCl_2$ were purchased from Alfa Inorganics.

2.2.13 Source of other simple salts/solvents/chemicals

Metal salts of AR grade were purchased from BDH /SRL/Aldrich/Sigma and used as such. All solvents and chemicals were also purchased from the aforesaid suppliers, and if necessary, were purified and dried before use.

2.3 Preparation of the Ligands

2.3.1 Preparation of N,N′-(2-hydroxy)propylenebis{(2-imino-3-oximino)butane}, H_2dampnol

The ligand was prepared by a previously published method [21]. Yield 70 %; m.p. 120 °C (lit. 121 °C).

Found: C, 53.19, H, 9.36, N, 21.57 %

Calculated for $C_{11}H_{24}N_4O_3$: C, 53.15, H, 9.29, N, 21.52 %

2.3.2 Preparation of N,N′-(2-hydroxy)propylenebis(acetylacetoneimine), H_2acacpnol

The ligand was prepared by a known method [22]. Yield 65 %; m.p. 101 °C (lit. 101-102 °C).

Found: C, 61.47, H, 8.73, N, 10.92 %

Calculated for $C_{13}H_{22}N_2O_3$: C, 61.42, H, 8.66, N, 11.02 %

2.3.3 Preparation of N,N′-(2-hydroxy)propylenebis(salicylaldimine), H_2salpnol

The ligand was prepared by the published literature method [22]. Yield 70 %; m.p. 99-101 °C (lit. 98-100 °C).

Found: C, 68.53, H, 6.12, N, 9.44 %

Calculated for $C_{17}H_{18}N_2O_3$: C, 68.45, H, 6.04, N, 9.39 %

2.3.4 Preparation of N,N′-(2-hydroxy)propylenebis(7-methylsalicylaldimine), H_2ohacpnol

The ligand was prepared by a previously published method [21]. Yield 70 %; m p. 112 °C (lit. 112 °C).

Found: C, 69.96, H, 6.83, N, 8.61 %

Calculated for $C_{19}H_{22}N_2O_3$: C, 69.92, H, 6.79, N, 8.58 %

2.3.5 Preparation of ligand, 1,2-di{(3-carboxyl)*o*-salicylaldiminophenylthio}ethane, (H_4dcsalpte)

This ligand was prepared by reacting 1,2-di(o-aminophenylthio)ethane (2.45 g, 9 mmol) with 3-formylsalicylic acid (2.988 g, 18 mmol) in ethanol (100 mL) under reflux (4 h). The yellow solid compound was recovered by filtration, washed with ethanol and dried over fused $CaCl_2$. The ligand is slightly soluble in MeOH, EtOH, highly soluble in DMSO and CH_3NO_2. Yield 75 %.

Found: C, 62.92, H, 4.22, N, 4.89 %

Calculated for $C_{30}H_{24}N_2O_6S_2$: C, 62.73, H, 4.26, N, 4.93 %

IR (KBr, cm^{-1}): 3440 cm^{-1} (ν_{PhOH}), 1680 cm^{-1} (ν_{COOH}) and 1620 cm^{-1} ($\nu_{C=N}$). UV-Vis. (DMSO, λ_{max}, nm (ε, L M^{-1} cm^{-1})): 285 (20,000), 370 (19800). ^{1}H NMR (d_6-DMSO, 300 MHz, ppm, 298 K): δ 8.7-9.0 (2H, s, C*H*=N), δ 6.8-8.5 2H, (m, 14 H, Ar-*H*), δ 2.75 (4H, s, –S–CH_2–CH_2–S–).

2.3.6 Preparation of 3-carboxy-2-hydroxybenzaldehyde morpholine N-thiohydrazone, H_2chbmth (thione form)

This ligand was prepared by a previously published method [23]. Yield 82 %, m.p. 186-187 °C (dec.) (lit. 185-187 °C (dec.))

Found: C, 50.56, H, 4.93, N, 13.52 %

Calculated for $C_{13}H_{15}N_3O_4S$: C, 50.48, H, 4.85, N, 13.54 %

2.3.7 Preparation of 1,8-N-bis(3-carboxy)disalicylidene-3,6-diazaoctane1,8-diamine, (H_4fsatrien)

3-Formylsalicylic acid (H_2fsa) (1.66 g, 10 mmol) was dissolved in methanol (25 mL) to which was added triethylenetetramine (0.73 g, 5 mmol) taken in methanol (20 mL) dropwise with stirring. Immediately a yellow solution was obtained. Glacial acetic acid (3/4 drops) was then added to it with stirring to facilitate completion of the condensation reaction and stirring continued for 6 h at –10 °C with the separation of a

yellow powdery compound at room temperature. It was filtered off, washed with methanol and ether and dried in *vacuo* over fused $CaCl_2$. Yield 25 %.

Found: C, 59.63; H, 5.89; N, 12.71 %

Calculated for $C_{22}H_{26}N_4O_6$: C, 59.72; H, 5.92; N, 12.66 %.

IR (KBr, cm^{-1}): 3412, 3290 (ν_{OH}, ν_{NH}), 1657 ($\nu_{C=N}$). UV-Vis. (DMSO, λ_{max}, nm (ε, L M^{-1} cm^{-1})): 265, 360, 495 (1128), 895 (23). ^{1}H NMR (d_6-DMSO, 300 MHz, ppm, 298 K). δ 8.94 (2H, s, C*H*=N), 7.91 (2H, d, Ar-*H*), 7.33 (2H, d, Ar-*H*), 6.67 (2H, t, Ar-*H*), 6.2 (2H, br, N*H*), 3.00-3.83 (8H, m, CH_2), 2.50-2.79 (4H, m, CH_2). ^{13}C NMR (d_6-DMSO, 300 MHz, ppm, 298 K): δ 172 (*C*OOH), 161.5 (*C*=N), 167.1, 139.1, 136.6, 130.3, 116.93, 114.09 (Ar-*C*), 51.2, 50.2, 49.15 (*C*H_2).

Due to the poor yield of the ligand, it was decided to use the metal-template procedure for the synthesis of complexes involving this ligand.

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