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# Synthesis and characterization of Mn(II) complexes of 4-phenyl(phenylacetyl)-3-thiosemicarbazide, 4-amino-5-phenyl-1,2,4-triazole-3thiolate, and their application towards electrochemical oxygen reduction reaction



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# ABSTRACT

Two new complexes,  $[Mn(ppt)_2(o-phen)]$  (1) and  $[Mn(aptt)(Cl)(o-phen)_2]$ ·2Haptt·H<sub>2</sub>O (2) with 4-phenyl (phenyl-acetyl)-3-thiosemicarbazide (Hppt) and 4-amino-5-phenyl-1,2,4-triazole-3-thiolate (Haptt) have been synthesized containing o-phenanthroline (o-phen) as a coligand. These complexes have been characterized by elemental analyses, IR and UV-Vis spectroscopic techniques, thermogravimetric analysis (TGA), magnetic susceptibility and single crystal X-ray diffraction data. The complexes are paramagnetic and have a distorted octahedral geometry. In complex 2, two molecules of Haptt and one water molecule are cocrystalized outside the coordination sphere. Complexes 1 and 2 are fluorescent and upon their excitation at 38 167 cm<sup>-1</sup>, exhibit emissions at 27 173 and 32 894 cm<sup>-1</sup>, respectively. TGA of complexes 1 and 2 indicate that the metal is converted into metal oxide at very high temperature. In the solid state, the crystal structure of both complexes are stabilized by various inter and intramolecular interactions. To explore the possible electrochemical applications of the complexes 1 and 2, they are immobilized on glassy carbon electrode using Nafion®. Cyclic voltammetry technique is used to characterize the metal complex immobilized electrodes in basic medium. Both complexes demonstrate excellent electrocatalytic activity towards electrochemical oxygen reduction. Since the electrocatalytic materials for oxygen reduction can dramatically increase the efficiency of the fuel cells and metal-air batteries, these metal complexes can be used as cathodic catalyst material in fuel cells and in metal-air batteries.

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# 1. Introduction

The coordination chemistry of manganese ion is the subject of current interest due to its involvement in a number of biological processes and in several catalytic applications. The complexes of manganese ions are of much interest because of its rich biochemistry and remarkable magnetic properties [1-3]. Thiosemicarbazide is the simplest representative of nitrogen sulfur containing ligands which is an emerging and rapidly developing area of research during the recent years [4-8]. Substituted thiosemicarbazides are used as intermediate for the synthesis of five membered nitrogen-sulfur or nitrogen-oxygen heterocyclic

\* Corresponding author. E-mail addresses: mkbharty@bhu.ac.in, manoj\_vns2005@yahoo.co.in (M.K. Bharty). compounds [9,10]. Thiosemicarbazide complexes have attracted much attention owing to their significant biological and medicinal properties [11–13]. 1,4-Disubstituted thiosemicarbazides are biologically versatile class of compounds exhibiting a variety of biological activities including antibacterial [14], antifungal [15], anti-inflammatory [16], antimyco-bacterial [17] and antimicrobial activities [18]. Acyl thiosemicarbazides are very important chelating agent and forms five membered bidentate or NNS/NNO tridentate complexes with metal ions [6]. In the presence of 1,10-phenanthroline, acyl thiosemicarbazides form N and O coordinated five membered bidentate complexes [4,17].

Acyl-thiosemicarbazide gets cyclized into 1,2,4-triazole-3thione in the presence of NaOH [18,19]. 1,2,4-Triazoles have extensively been used as antibacterial, antifungal, antimicrobial, antitumor, anti-inflammatory, anti-malarial, antioxidant, antileishmanial, antiviral and herbicide agents [20,21]. 1,2,4-Triazole3-thione exists in tautomeric equilibrium in solution which enables two possible configurations of the -NHCS moiety as thione and thiol forms (Scheme 1). This tautomerism causes the proton transfer or migration on the triazole ring and consequently the ligand binds in various coordination modes with different metal ions [22]. The mercapto group can act as a donor site exhibiting uninegative monodentate or neutral bridging modes between two metal centres or as a bridge between three metal centres in the azolato or thiolato form in thiol form, while on complexation with ring nitrogen, only the thione form of the ligands exists in the solid state [23]. Metal complexes containing 1,10-phenanthroline have attained much importance due to their versatile roles as building blocks for the synthesis of metallo-dendrimers and as molecular scaffolding for supramolecular assemblies. They also find applications in ring-opening metathesis polymerization, biochemistry analytical chemistry, electrochemistry and in catalysis [24.25]. Oxygen reduction reaction (ORR) possesses a significant role in the development of fuel cells [26–28]. In the fuel cells, oxygen is electrochemically reduced to water via four electron transfer process [29,30]. However, lack of efficient ORR catalyst limits the efficiency of all types of fuel cells [28]. The necessity of costeffective ORR catalysts becomes the constant driving force for the scientific and industrial research worldwide [26-28] for the development of new ORR catalysts. In view of the above facts, we have synthesized and fully characterized two new complexes 1 and 2. Further, these complexes are immobilized on glassy carbon electrodes, and used for the electrochemical ORR.

## 2. Experimental

### 2.1. Materials and methods

All commercial reagents were of reagent grade (Sigma-Aldrich/ SD Fine) and used as received. All the synthetic manipulations were carried out in an open atmosphere at room temperature. The solvents were dried and distilled before use following the standard procedures. N,N'-Dimethylformamide (DMF) was purchased from SD-Fine Chemicals, India. Nafion® (5 wt% dissolved in lower aliphatic alcohols), abbreviated as Nf was procured from Sigma-Aldrich, India. It was diluted to 0.01% using ethanol to coat on the surface of the electrode. Potassium hydroxide (KOH) was purchased from Merck, India. Excel pure nitrogen was used for the inert condition in electrochemical cell. The synthesis and characterization of 4-phenyl(phenyl-acetyl)-3-thiosemicarbazide (Hppt) and 4-amino-5-phenyl-1,2,4-triazole-3-thione (Haptt) are described elsewhere [31,32].

#### 2.2. Physical measurements

Carbon, hydrogen and nitrogen contents were determined on a CHN Model CE-440 Analyzer while sulfur was estimated as BaSO<sub>4</sub>. IR spectra were recorded in the 4000–400 cm<sup>-1</sup> region on a "PerkinElmer Spectrum Two" FT-IR spectrophotometer as KBr pellets. Magnetic susceptibility measurements were performed at room temperature on a Cahn Faraday balance using Hg[Co(NCS)<sub>4</sub>] as



Scheme 1. Thiol and thione forms of Haptt ligand.

the calibrant. The electronic spectra were recorded on a SHIMADZU 1700 UV–vis spectrophotometer in methanol. The fluorescent data were collected at room temperature on "Agilent Technologies Cary Eclipse" Fluorescence Spectrophotometer in MeOH. Thermogravimetric analyses (TGA) were performed using a Perkin Elmer-STA 6000 thermal analyzer in a N<sub>2</sub> atmosphere at a heating rate of 10 °C min<sup>-1</sup>

# 2.3. Cyclic voltammetry

Hydrodynamic voltammetry measurements were carried out using rotating disc electrode (RDE) setup from Pine research instruments, USA. Glassy carbon rotating disc electrode ( $GC_{RDE}$ ) with a diameter of 5 mm is used for the hydrodynamic voltammetry. The electrochemical measurements were recorded using CH Instruments (CHI-660C, USA) electrochemical workstation. The glassy carbon (GC) electrode (3 mm diameter) or GC<sub>RDE</sub> as working electrode, platinum wire as counter electrode, and saturated calomel electrode (SCE) as reference electrode were used for electrochemical experiments. However, the potentials are converted to reversible hydrogen electrode (RHE) potential and guoted throughout the manuscript unless otherwise indicated. All the electrochemical experiments were performed using triple distilled water. For the preparation of oxygen or nitrogen saturated conditions in the electrochemical cell, continuous purging of the respective gas was performed for 20 minutes. Cyclic voltammetry technique is used to characterize the complex immobilized electrodes in basic medium (0.1 M aqueous KOH).

#### 2.4. Immobilization of metal complex

Nf solution in ethanol (5.0  $\mu$ L) was coated on GC electrode and kept for 30 min to dry at room temperature condition. This Nf coated GC electrode (GC/Nf) was dipped into the metal complex (**1**) solution (5 mM in DMF) for 1 h. Then the electrode was removed from the solution, washed with triple distilled water (abbreviated as GC/Nf/[Mn(ppt)<sub>2</sub>(o-phen)]) and utilized for the electrochemical measurements. Similar steps were performed for the preparation of GC/Nf/[Mn(aptt)(Cl)(o-phen)<sub>2</sub>]·2Haptt·H<sub>2</sub>O electrode also. GC<sub>RDE</sub>/Nf electrodes were prepared similarly however, coating with 14.0  $\mu$ L of 0.01% Nf solution. Immobilization of the complexes was done similar to the above procedures and represented as GC<sub>RDE</sub>/Nf/[Mn(ppt)<sub>2</sub>(o-phen)] and GC<sub>RDE</sub>/Nf/[Mn(aptt) (Cl)(o-phen)<sub>2</sub>]·2Haptt·H<sub>2</sub>O.

## 2.5. X-ray crystallography

Crystals suitable for X-ray analyses of complexes **1** and **2** were grown at room temperature. Single crystal X-ray diffraction data collection for complex **1** was performed on an Xcalibur, Eos, Gemini diffractometer equipped with CrysAlis Pro., using a copper monochromated Cu K $\alpha$  ( $\lambda$  = 1.54178 Å) radiation source at 173(2) K whereas for complex **2**, Bruker APEX-II CCD diffractometer equipped with a SMART 6000 detector at room temperature with a graphite monochromated Mo K $\alpha$  ( $\lambda$  = 0.71073 Å) radiation source at 293 K was used. Multi-scan absorption correction was applied to the X-ray data of both compounds. The structure was solved by direct methods (SHELXL-2013) and refined by full matrix least-square on  $F^2$  (SHELXL) using anisotropic displacement parameters for all non-hydrogen atoms. All hydrogen atoms were included in calculated position and refined with a riding model [33]. Figures were drawn using the programs MERCURY and ORTEP-3 [34,35].

# 3. Syntheses

#### 3.1. Synthesis of $[Mn(ppt)_2(o-phen)]$ (1)

A solution of Hppt (0.386 g, 2 mmol) in MeOH (10 mL) was added to a methanol solution (10 mL) of  $Mn(OAc)_2 \cdot 4H_2O$ (0.245 g, 1 mmol) and the reaction mixture was stirred for 3 h at room temperature. The resulting precipitate obtained was filtered off and washed with methanol. A methanol solution of *o*-phen was added slowly into the methanol suspension of the above compound and stirred for 1 h. A yellow color solution obtained was filtered off and kept for crystallization. Yellow crystals of **1** suitable for X-ray analyses were obtained by slow evaporation of the methanol solvent over a period of 15 days. Yield: 65%, m.p. 183 °C. Anal. Found: C, 62.40; H, 4.60; N, 13.75; S, 8.05%. Calc. for C<sub>42</sub>H<sub>36</sub>MnN<sub>8</sub>O<sub>2</sub>S<sub>2</sub> (803.85): C, 62.75; H, 4.51; N, 13.93; S, 7.97%. IR (KBr, cm<sup>-1</sup>): v(N-H) 3183, v(C-H) 3051–2924, v(C=O) 1633, v(N-N) 1050, v(C=S) 992, v(Mn-N) 485, v(Mn-O) 419.

# 3.2. Synthesis of [Mn(aptt)(Cl)(o-phen)<sub>2</sub>]·2Haptt·H<sub>2</sub>O (2)

A solution of Haptt (0.570 g, 3 mmol) in MeOH (10 mL) was added to a methanol solution (10 ml) of  $MnCl_2 \cdot 4H_2O$  (0.198 g, 1 mmol) and the reaction mixture was stirred for 3 h at room temperature. The resulting precipitate obtained was filtered off and washed with methanol. A methanol solution of *o*-phen was added slowly into the methanol suspension of the above compound and stirred for 1 h. A yellow color solution obtained was filtered off and kept for crystallization. Yellow crystals of **2** suitable for X-ray analyses were obtained over a period of 15 days. Yield: 72%, m.p. 172 °C. Anal. Found: C, 55.28; H, 3.75; N, 21.42; S, 9.08%. Calc. for  $C_{48}H_{41}ClMnN_{16}OS_3$  (1044.54): C, 55.19; H, 3.95; N, 21.45; S, 9.21%. IR (KBr, cm<sup>-1</sup>):  $\nu$ (O–H) 3417,  $\nu$ (N–H) 3190, 3261,  $\nu$ (C–H) 3046–2924,  $\nu$ (C=N) 1609,1587;  $\nu$ (N–N) 1036,1050;  $\nu$ (C=S) 951,  $\nu$ (C–S) 883,  $\nu$ (Mn–N) 509,  $\nu$ (Mn–S) 411.

# 4. Results and discussion

The ligand 4-phenyl (phenyl-acetyl)-3-thiosemicarbazide (Hppt) and 4-amino-5-phenyl-1,2,4-triazole-3-thione (Haptt) reacts with Mn(OAc)<sub>2</sub>·4H<sub>2</sub>O/MnCl<sub>2</sub>·4H<sub>2</sub>O and forms light yellow precipitates in methanol solution. The above precipitate was dissolved in methanolic solution of o-phenanthroline to form octahedral complexes [Mn(ppt)<sub>2</sub>(o-phen)] (1) and [Mn(aptt)(Cl)  $(o-phen)_2$ ]·2Haptt·H<sub>2</sub>O (**2**), respectively. Acyl thiosemicarbazide (RCONHNHCSNHR) gets cyclized very easily into their corresponding oxadiazoles when treated with weak acid or weak base [36] or manganese(II) acetate [37] via loss of H<sub>2</sub>S. However, the similar acyl-thiosemicarbazide treated with strong acid/metal nitrate gets converted into corresponding thiadiazole via loss of H2O (Scheme 2) instead of oxadiazoles [38]. Often without any reactant acyl-thiosemicarbazide gets converted into its corresponding oxdiazole with due course of time in the presence of air. Thus for the prevention of self cyclization, freshly prepared acyl-thiosemicarbazide should be used for complexation with metal ion [16]. Acyl/aroyl-thiosemicarbazide gets converted into 1,2,4-triazole-3thione in the presence of strong base NaOH (Scheme 2) [18,19]. The complex 2 obtained from the tautomerization of the ligand with subsequent deprotonation. Schemes 3 and 4 depict the formation of ligand 4-phenyl (phenyl-acetyl)-3-thiosemicarbazide (Hppt) and 4-amino-5-phenyl-1,2,4-triazole-3-thiolate (Haptt) and their complexes [Mn(ppt)<sub>2</sub>(o-phen)] (1) and [Mn(aptt)(Cl)(ophen)<sub>2</sub>]·2Haptt·H<sub>2</sub>O (**2**) containing o-phen as coligand. Complexes 1 and 2 melt at 184 and 172 °C, respectively. The complexes are insoluble in common organic solvents but are soluble in DMF and DMSO.

### 4.1. IR spectra

The IR spectrum of [Mn(ppt)<sub>2</sub>(o-phen)] (**1**) shows absorptions  $(cm^{-1})$  due to the stretching modes of NH (3183), C=O (1633), N–N (1050), C=S (992), respectively. [Mn(ppt)<sub>2</sub>(o-phen)] (1) shows the absence of v(N-H) band at  $\sim$ 3224 cm<sup>-1</sup> (present in the ligand) indicating loss of hydrogen from the nitrogen of thioamide group which is supported by a small positive shift of 18 cm<sup>-1</sup> in v(N-N). A negative shift of about 35 cm<sup>-1</sup> in v(C=0) indicating bonding through the carbonyl oxygen to the metal ion [39]. The appearance of two new bands at 485 and 419 cm<sup>-1</sup> suggest formation of M-N and M-O bonds. The IR spectrum of [Mn(aptt)(Cl)(ophen)<sub>2</sub>]·2Haptt·H<sub>2</sub>O (2) shows absorptions (cm<sup>-1</sup>) due to the stretching modes of N-H (3261), C=N (1587), N-N (1036), C=S (951), respectively. The occurrence of one OH stretching band in the spectrum of complex 2 indicates the presence of water molecule. The IR spectrum of [Mn(aptt)(Cl)(o-phen)<sub>2</sub>]·2Haptt·H<sub>2</sub>O (2) shows one band at 3261 cm<sup>-1</sup> due to v(NH) of triazole NH<sub>2</sub> group and the loss of one triazole NH group upon complexation. Thus, it is clear from the IR data that the ligand acts as a uni-negative monodentate in complex 2, bonding through one triazole thiolato sulfur (conversion of thione sulfur to thiolato sulfur). A negative shift of 67 cm<sup>-1</sup> in v(C=S) in complex **2** indicates conversion of C=S bond to C-S. The appearance of new bands near 509 and 411 cm<sup>-1</sup> suggest formation of M–N and M–S bonds in complex 2. In addition, IR spectrum of complex 2 shows four absorptions  $(cm^{-1})$  due to the stretching modes of N–H (3190), C=N (1609), N–N (1050) and C=S (951), respectively indicating the presence of two uncoordinated cocrystallized ligand molecules. The C-H stretching vibrations of methyl group are observed in the range 2724 to 2919  $\text{cm}^{-1}$  in the spectra of the ligands and complexes **1** and **2**.

## 4.2. Crystal structure descriptions

The molecular structures of complexes **1** and **2** were obtained using single crystal X-ray diffraction data. The crystallographic data and structural refinement details are listed in Table 1. Selected bond lengths and angles are given in Tables 2 and 3. Hydrogen bonding parameters for complexes **1** and **2** are given in Tables 4 and 5.

### 4.2.1. Crystal structure of [Mn(ppt)<sub>2</sub>(o-phen)] (1)

Fig. 1 shows the molecular structure of  $[Mn(ppt)_2(o-phen)]$  (1) together with the atom labeling scheme. The coordination sphere of complex 1 is fulfilled by two amide carbonyl oxygen and a deprotonated hydrazine nitrogen atom of two uni-negative bidentate ppt ligands and two nitrogen atoms of o-phen; forming three five membered chelate rings. The bite angles in five membered chelate rings with ppt  $\{O(1)-Mn-N(2) = 74.63(6)^{\circ}\}$  and o-phen  $\{N(4)#1-Mn-N(4) = 73.18(10)^{\circ}\}$  ligands exhibit substantial deviation from ideal octahedron angle (90°) suggesting a distorted octahedral geometry around Mn(II) (Table 2). The six-coordinate geometry at the manganese(II) centre is described as distorted octahedral on account of the considerable ligand imposed deviations of the *cis* and *trans* angles from the idealized octahedral angles (90 and 180°, respectively). Similarly, the trans angles also vary significantly O(1)-Mn-O(1) (156.07) from an ideal angle of 180°. The hydrazine nitrogen Mn–N bonds distances are slightly shorter than the o-phen nitrogens indicating that the hydrazinic nitrogen bonds stronger than the *o*-phen nitrogen atoms [40]. The manganese atom in complex **1** is located on a twofold axis which passes through the middle of C21-C21' bond. The bond



Scheme 2. Cyclization of acyl/aroyl thiosemicarbazide.



Scheme 3. Synthesis of [Mn(ppt)<sub>2</sub>(o-phen)] (1).



Scheme 4. Synthesis of [Mn(aptt)(Cl)(o-phen)<sub>2</sub>]·2Haptt·H<sub>2</sub>O (2).

angles and distances are very similar to those reported earlier for octahedral Mn(II) complexes [41,42]. Due to coordination with metal ion C—O bond distance (1.253 Å) in complex **1** is longer than

that of free Hppt (1.226–1.231 Å) while C=S bond distances are almost similar in free Hppt ligand and complex [43]. The carbon sulfur bond distance [1.703(2) Å] suggests C=S double bond

| Table 1                             |   |     |    |
|-------------------------------------|---|-----|----|
| Crystallographic data for complexes | 1 | and | 2. |

| Parameters                                    | 1                              | 2                              |
|---|--------------------------------|--------------------------------|
| Empirical formula                             | $C_{42}H_{36}MnN_8O_2S_2$      | C48H41ClMnN16OS3               |
| Formula weight                                | 803.85                         | 1044.54                        |
| Crystal system                                | monoclinic                     | triclinic                      |
| Space group                                   | C2/c                           | $P\overline{1}$                |
| T (K)   | 173(2)                         | 293(2)                         |
| λ, Cu Kα (Å)/Mo Kα (Å)                        | 1.54178                        | 0.71073                        |
| Unit cell dimensions                          |                                |                                |
| a (Å)   | 21.3463(7)                     | 11.1905(4)                     |
| b (Å)   | 9.9913(3)                      | 11.2247(4)                     |
| c (Å)   | 19.0870(7)                     | 19.3447(7)                     |
| α (°)   | 90                             | 100.693(3)                     |
| β (°)   | 106.437(3)                     | 95.117(3)                      |
| γ(°)  | 90                             | 90.310(3)                      |
| $V(Å^3)$                                      | 3904.5(2)                      | 2377.58(15)                    |
| Z   | 4                              | 2                              |
| $\rho_{\text{Calc.}}$ (g cm <sup>3</sup> )    | 1.367                          | 1.459                          |
| $\mu$ (mm $^{-1}$ )                           | 4.132                          | 0.523                          |
| F(0 0 0)                                      | 1668                           | 1078.0                         |
| Crystal size (mm)                             | $0.53 \times 0.42 \times 0.16$ | $0.25 \times 0.18 \times 0.15$ |
| $\theta$ range for data collections (°)       | 4.319-71.236                   | 2.853-29.153                   |
| Index ranges                                  | $-26 \leq h \leq 26$ ,         | $-13 \le h \le 15$ ,           |
|   | $-12 \leq k \leq 7$ ,          | $-14 \leq k \leq 15$ ,         |
|   | $-23 \le l \le 16$             | $-25 \le l \le 26$             |
| Number of reflections collected               | 7327                           | 20 197                         |
| Number of independent reflections $(R_{int})$ | 3805                           | 12 851                         |
| Number of data/                               | 3805/0/258                     | 12 851/0/639                   |
| Goodness-of-fit (GOF) on $F^2$                | 1 039                          | 1 024                          |
| $R_1^{a} W R_2^{b} [(I > 2\sigma(I)]]$        | 0.0437 0.1158                  | 0.0653 0.1237                  |
| $R_1^a w R_2^b$ (all data)                    | 0.0503 0.1205                  | 01254 01510                    |
| Largest difference in peak/hole               | 0.536 - 0.510                  | 0.389 - 0.515                  |
| $(e Å^{-3})$                                  | 0.010                          | 0.000, 0.010                   |

<sup>a</sup>  $R_1 = \Sigma ||F_0| - |F_0| \Sigma |F_0|$ .

<sup>b</sup>  $R_2 = [\Sigma w(|F_0^2| - |F_c^2|)^2 / \Sigma w |F_0^2|^2]^{1/2}.$ 

#### Table 2

| Selected interatomic distances and a | angles for | [Mn(ppt] | ) <sub>2</sub> (o-p | hen)] | (1 | 1) |
|--------------------------------------|------------|----------|---------------------|-------|----|----|
|--------------------------------------|------------|----------|---------------------|-------|----|----|

| Bond length (Å) |          | Bond angle (°)      |            |
|-----------------|----------|---------------------|------------|
| Mn-0(1)         | 2.158(2) | O(1)-Mn-O(1)#1      | 156.07(10) |
| Mn-N(2)         | 2.244(2) | O(1)– $Mn$ – $N(2)$ | 74.63(6)   |
| Mn-N(4)         | 2.269(2) | O(1)-Mn-N(2)#1      | 91.75(6)   |
| S(1)-C(7)       | 1.703(2) | O(1)– $Mn$ – $N(4)$ | 106.65(6)  |
| O(1)-C(8)       | 1.253(3) | O(1)-Mn-N(4)#1      | 92.66(6)   |
| N(1)-C(7)       | 1.369(3) | N(2)-Mn-N(2)#1      | 111.11(9)  |
| N(1)-C(1)       | 1.414(3) | N(2)– $Mn$ – $N(4)$ | 161.01(7)  |
| N(2)-C(7)       | 1.335(3) | N(2)-Mn-N(4)#1      | 87.86(7)   |
| N(2)-N(3)       | 1.393(3) | N(4)#1-Mn-N(4)      | 73.18(10)  |
| N(3)-C(8)       | 1.318(3) | N(2) - C(7) - N(1)  | 112.14(18) |
| C(1)-C(6)       | 1.383(4) | N(2) - C(7) - S(1)  | 124.34(17) |
| C(1)-C(2)       | 1.386(4) | N(1)-C(7)-S(1)      | 123.52(16) |
| C(8)-C(9)       | 1.513(3) | O(1)-C(8)-N(3)      | 121.80(20) |
| C(9)-C(10)      | 1.505(4) | O(1) - C(8) - C(9)  | 120.70(20) |
| N(4)—C(16)      | 1.331(3) | N(3)-C(8)-C(9)      | 117.50(20) |

Symmetry transformations used to generate equivalent atoms: #1 -x + 1, y, -z + 3/2.

character which remains uncoordinated and takes part in C–H $\cdots$ S and N–H $\cdots$ S hydrogen bonding leading to a supramolecular structure (Table 4).

# 4.2.2. Crystal structure of [Mn(aptt)(Cl)(o-phen)<sub>2</sub>]·2Haptt·H<sub>2</sub>O (2)

Fig. 2 shows the molecular structure of  $[Mn(aptt)(Cl)(o-phen)_2]$ -2Haptt·H<sub>2</sub>O (**2**) together with the atom numbering scheme. In complex **2**, the coordination sphere of Mn(II) is fulfilled by four nitrogen atoms of two units of *o*-phen, one thiolato sulfur atom of uni-negative monodentate aptt ligand and one chloride ion. The Haptt ligand exist in the thiol form in coordination sphere of

Selected interatomic distances and angles for [Mn(aptt)Cl(o-phen)<sub>2</sub>]2Haptt·H<sub>2</sub>O (2).

| 5) 153.59(10) |
|---------------|
| 4) 72.70(10)  |
| 4) 90.16(10)  |
| 6) 86.72(10)  |
| 5) 71.57(10)  |
| 6) 85.05(10)  |
| 102.21(7)     |
| 96.84(8)      |
| 87.61(7)      |
| 166.22(8)     |
| 98.04(7)      |
| 96.90(8)      |
| 169.74(8)     |
| 90.10(8)      |
| 98.88(4)      |
|               |

complex 2 in which metal is bonded through thiolato sulfur whereas two uncoordinated co-crystallized Haptt molecules are present in the thione form. One water molecule is also cocrystallized outside the coordination sphere. The crystal structure of complex 2 reveals that the Mn(II) complex with aptt ligand resulted from tautomerization of ligand Haptt with subsequent deprotonation. There is a significant disparity in the Mn(II)–N bond distances of each o-phen ligand, indicating the trans-influence of the thiolate and chloride donor atoms. The *o*-phen nitrogen atom opposite to the thiolate sulfur atom and the chloride atom are somewhat elongated in accordance with the trans-influence. As usual, both ophen ligands form five member MnN<sub>2</sub>C<sub>2</sub> chelate rings. The bite angles in o-phen chelate rings (71.57° and 72.70°) are shorter than 90° due to the geometrical constrains inside the chelate ring. The Mn-Cl (2.453 Å) bond distance is similar with other reported Mn–Cl bond distances [44]. The bite angles and other angles between coordination bonds;  $N(15)-Mn(1)-N(14) = 90.16(10)^{\circ}$ ,  $N(13)-Mn(1)-N(16) = 86.72(10)^{\circ}, N(14)-Mn(1)-N(16)^{\circ} = 85.05$ (10)° suggest a distorted octahedral geometry around Mn(II) ion (Table 3). The carbon sulfur bond distances present in uncoordinated Haptt ligand  $\{S(3)-C(15) = 1.687(4) \text{ Å}, S(2)-C(24) =$ 1.663 Å} are shorter than C–S single bond distance (1.719(4) Å) of coordinated aptt ligand suggesting double bond character in the uncoordinated unit [45] and the manganese sulfur bond distance is 2.584(11) Å. Thus, the coordinated ligand is present in thiol form. In solid state, the crystal structure of complex 2 is stabilized by various inter and intra molecular hydrogen bonding interactions (Table 5). The water molecule present in crystal lattice also stabilized the crystal packing. In addition, weak C–H $\cdots$  $\pi$ (3.239 and 3.344 Å) and  $\pi \cdots \pi$  (3.785 Å) interactions are also present in the complex 2.

# 4.3. Magnetic moments and electronic spectra

The magnetic moment value of 5.87 and 5.95 B.M. for [Mn (ppt)<sub>2</sub>(*o*-phen)] (1) and [Mn(aptt)(Cl)(*o*-phen)<sub>2</sub>]·2Haptt·H<sub>2</sub>O (2) suggest the presence of high spin Mn(II) with five unpaired electrons. The electronic spectra of complexes 1 and 2 show two bands at 264, 315 ( $\varepsilon$  = 65 800 and 6500 LM<sup>-1</sup> cm<sup>-1</sup>) and 263 and 325 nm ( $\varepsilon$  = 62 100 and 2100 LM<sup>-1</sup> cm<sup>-1</sup>), respectively which may be assigned to the intraligand/charge transfer transitions (Fig. 3) [46].

# 4.4. Photoluminescence studies

The photoluminescent properties of Hppt, Haptt and complexes **1** and **2** are recorded in methanol  $(10^{-5} \text{ M})$ , It shows that these compounds have characteristic fluorescence emissions. The absorption spectra and photoluminescence emission spectra of

#### Table 4

Inter and intramolecular interactions [Å and °] for complex 1.

| D—H···A                   | d(D—H) | $d(H \cdots A)$ | $d(D \cdots A)$ | <(DHA) |
|---------------------------|--------|-----------------|-----------------|--------|
| N(1)—H(1N)O(1)#1          | 0.90   | 2.04            | 2.930(3)        | 168    |
| N(3)—H(3N)S(1)            | 0.78   | 2.37            | 2.852(2)        | 120    |
| $C(6) - H(6A) \dots S(1)$ | 0.95   | 2.71            | 3.206(3)        | 113    |
| C(16)—H(16A)N(2)#1        | 0.95   | 2.59            | 3.197(3)        | 122    |

Symmetry transformations used to generate equivalent atoms: #1 - x + 1, y, -z + 3/2.

#### Table 5

Inter and intramolecular interactions [Å and °] for complex 2.

| D—H···A             | d(D—H) | $d(H \cdots A)$ | $d(D{\cdots}A)$ | <(DHA) |
|---------------------|--------|-----------------|-----------------|--------|
| N(9)—H(9A)O(1)#1    | 0.86   | 1.94            | 2.725(5)        | 152    |
| N(6)-H(6A)N(2)#2    | 0.86   | 1.95            | 2.800(4)        | 170    |
| N(8)—H(8A)N(8)#3    | 0.86   | 2.58            | 3.020(7)        | 112    |
| N(8)—H(8B)S(3)#3    | 0.86   | 3.01            | 3.415(4)        | 111    |
| N(8)-H(8B)N(10)#4   | 0.86   | 2.61            | 3.021(5)        | 110    |
| C(035)—H(035)Cl     | 0.93   | 2.96            | 3.577(4)        | 125    |
| C(060)-H(060)N(7)#1 | 0.93   | 2.63            | 3.330(5)        | 132    |
| O(1)—H(50)S(3)#5    | 0.80   | 2.52            | 3.309(4)        | 168    |
| O(1)-H(51)N(1)      | 0.79   | 1.99            | 2.782(5)        | 174    |

Symmetry transformations used to generate equivalent atoms: #1 - x + 1, -y + 1, -z + 1; #2 x - 1, y, z; #3 - x, -y, -z; #4 x, y - 1, z - 1; #5 x + 1, y, z.



Fig. 1. Molecular structure of  $Mn(ppt)_2(o-phen)$ ] (1) at 30% ellipsoids probability level.

complexes are shown in Figs. 3 and 4. Complexes **1** and **2** exhibit a slightly higher luminescent property as compared to the free ligands, Hppt and Haptt with respect to intensity and energy. The ligands, Hppt and Haptt exhibit emission maxima at 27 247 and 26 315 cm<sup>-1</sup> upon excitation at 38 167 cm<sup>-1</sup>. Complexes **1** and **2**, upon excitation at 38 167 cm<sup>-1</sup>, exhibit emission maxima at 27 173 and 32 894 cm<sup>-1</sup>, respectively. Thus Hppt, Haptt, and complexes **1** and **2** show Stokes shift of 10 920, 11 852, 10 994 and 5273 cm<sup>-1</sup>, respectively and emit blue light. The emission spectra suggest that complexes **1** and **2** exhibit slightly intense emission as compared to free ligands. It is reported that, those complexes having electron-donating groups on the triazole ring showed a high intensity emission in the green region with respect to the other complexes. It can be explained by the electron donating characters of the substituent present on the triazole which raises the



Fig. 2. Molecular structure of  $[Mn(aptt)Cl(o-phen)_2]$ ·2Haptt·H<sub>2</sub>O (2) at 30 % ellipsoids probability level.

energy of the HOMO level of the triazole complex. The above explanation further conclude that the substitution on the triazole ring represents a small perturbation to the energy levels and the electron-donating or withdrawing ability of the substituents on the triazole can change the emission properties [47,48]. The main chromospheres in the complex **2** are the five membered triazole rings and its conjugation degree is further enhanced by the phenyl ring. The involvement of carbonyl oxygen and hydrazine nitrogen in binding with Mn(II) ions and an increased rigidity in structure of complexes **1** and **2** are the possible reasons for the increase in the photoluminescence. Hence, complexes **1** and **2** may serve as a potential photoactive material as indicated from its characteristic fluorescence properties.

# 4.5. Thermal studies

Thermal properties of [Mn(ppt)<sub>2</sub>(*o*-phen)] (**1**) and [Mn(aptt)(Cl) (*o*-phen)<sub>2</sub>]·2Haptt·H<sub>2</sub>O (**2**) were studied by controlled heating at

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Fig. 3. UV–Vis absorption spectra of Hppt, Haptt, complexes 1 and 2 at  $10^{-5}$  M in MeOH.



**Fig. 4.** Emission spectra of Hppt, Haptt, complexes **1** and **2** at  $10^{-5}$  M in MeOH. (Excitation wavelength for Hppt, Haptt, complexes **1** and **2** were 263, 255, 265 and 263 nm, respectively.)

the rate of 10 °C min<sup>-1</sup> in the temperature range 30–900 °C under a N<sub>2</sub> atmosphere. The stability of complexes are decided by the coordinated ligands as well as hydrogen bonding which is one of the most important non-covalent interactions and plays an important role in building the supramolecular structures and thus making a great contribution to thermal stabilities [49]. Thermogram of complex 1 reveals that the compound decomposes around 100 °C (Fig. 5). Complex 1 decomposed continuously in three ambiguous steps in the temperature ranges 100-225, 225-500 and 500-900 °C due to loss of organic moiety and finally metal is converted into the metal oxide (MnO) at higher temperature. (Calc. weight loss 10.81%; obs. 10.72%) [49]. Complex 2 is less stable than complex 1 and decomposed in three distinct steps in the temperature ranges 60-120, 120-500 and 500-900 °C (Fig. 6). The first minor weight loss may be due to the loss of water molecule and chlorine atom (Calc. weight loss 5.12%; obs. 6.05%). Upto 500 °C more than 85% weight of complex 2 was decomposed due to breakdown of organic moieties, and finally, metal is converted into its oxide at 900 °C.



Fig. 5. Thermogram of complex 1.



Fig. 6. Thermogram of complex 2.

# 4.6. Electrochemical characterizations

The metal complex immobilized electrodes, GC/Nf/[Mn(ppt)<sub>2</sub>(ophen)] and GC/Nf/[Mn(aptt)(Cl)(o-phen)<sub>2</sub>]·2Haptt·H<sub>2</sub>O were characterized using cyclic voltammetry in 0.1 M KOH at 20 mV s<sup>-1</sup> (Fig. 7A). GC/Nf electrode (curve a of Fig. 7A) does not display any characteristic redox peak in 0.1 M KOH. GC/Nf/[Mn(ppt)<sub>2</sub>(ophen)] (curve b of Fig. 7A) displays reduction and oxidation peaks at 1.10 and 1.38 V (versus RHE), correspond to Mn(II)/Mn(0) and Mn(0)/Mn(II) electrochemical process, respectively, GC/Nf/ [Mn (aptt)(Cl)(o-phen)<sub>2</sub>]·2Haptt·H<sub>2</sub>O (curve c of Fig. 7A) displays broad redox peaks at 1.02 and 1.28 V (versus RHE), due to Mn(II)/Mn(0) and Mn(0)/Mn(II) redox process, respectively [50-53]. The less intense redox peaks at both electrodes, GC/Nf/[Mn(ppt)<sub>2</sub>(o-phen)] and GC/Nf/[Mn(aptt)(Cl)(o-phen)<sub>2</sub>]·2Haptt·H<sub>2</sub>O are probably due to a non-favorable redox process of Mn(II) [50-53]. Since the stability of Mn(I) is very less, the reduction process, Mn(II) to Mn(I) is less favored and accordingly, the reduced Mn(I) is further



**Fig. 7.** (A) Cyclic voltammetry response of GC/Nf (a), GC/Nf/[Mn(ppt)<sub>2</sub>(o-phen)] (b), and GC/Nf/[Mn(aptt)Cl(o-phen)<sub>2</sub>]-2Haptt-H<sub>2</sub>O (c) electrodes with a scan rate of 20 mVs<sup>-1</sup> in 0.1 M KOH. (B) LSV curve of GC<sub>RDE</sub>/Nf/[Mn(ppt)<sub>2</sub>(o-phen)] (b), and GC<sub>RDE</sub>/Nf/[Mn(aptt)Cl(o-phen)<sub>2</sub>]-2 Haptt-H<sub>2</sub>O (c) electrodes in 0.1 M KOH with a scan rate of 10 mV s<sup>-1</sup> and a rotation rate of 1600 rpm.

converted to Mn(0). Therefore, the observed redox peaks are corroborated to Mn(II)/Mn(0) and Mn(0)/Mn(II), respectively. The experimental evidence for the Mn(II) to Mn(0) is well documented based on the polarographic measurements [51]. Further, these electrodes are utilized for ORR in 0.1 M aqueous KOH solution (*vide infra*).

### 4.7. Electrochemical oxygen reduction reaction

ORR was analyzed using linear sweep voltammetry (LSV) technique at GC<sub>RDE</sub> in 0.1 M KOH (scan rate 10 mVs<sup>-1</sup>) with a constant rotation rate of 1600 rpm (Fig. 7B). All three electrodes, GC<sub>RDE</sub>/Nf,  $GC_{RDE}/Nf/[Mn(ppt)_2(o-phen)]$  and GC<sub>RDE</sub>/Nf/[Mn(aptt)(Cl)(ophen)<sub>2</sub>]·2Haptt·H<sub>2</sub>O represents very low/negligible reduction current in nitrogen saturated condition (curves a'-c' respectively, of Fig. 7B). However, a significant reduction current was observed in the oxygen saturated condition (curves a-c respectively, of Fig. 7B), indicating the electrocatalytic ORR [28,29]. The onset potential for ORR at GC<sub>RDE</sub>/Nf, GC<sub>RDE</sub>/Nf/[Mn(ppt)<sub>2</sub>(o-phen)] and GC<sub>RDE</sub>/Nf/[Mn(aptt)(Cl)(o-phen)<sub>2</sub>]·2Haptt·H<sub>2</sub>O is measured as 0.73, 0.78 and 0.81 V (versus RHE), respectively. The positive shift of ORR onset potential at GC<sub>RDE</sub>/Nf/[Mn(ppt)<sub>2</sub>(o-phen)] and GC<sub>RDE</sub>/ Nf/[Mn(aptt)(Cl)(o-phen)<sub>2</sub>]·2Haptt·H<sub>2</sub>O compared to GC<sub>RDE</sub>/Nf represents an efficient ORR activity at GC<sub>RDE</sub>/Nf/[Mn(ppt)<sub>2</sub>(o-phen)] and GC<sub>RDE</sub>/Nf/[Mn(aptt)(Cl)(o-phen)<sub>2</sub>]·2Haptt·H<sub>2</sub>O. Further, the ORR onset potential of GC<sub>RDE</sub>/Nf/[Mn(ppt)<sub>2</sub>(o-phen)] is +20 mV higher than GC<sub>RDE</sub>/Nf/[Mn(aptt)(Cl)(o-phen)<sub>2</sub>]·2Haptt·H<sub>2</sub>O indicating the superior activity of GC<sub>RDE</sub>/Nf/[Mn(ppt)<sub>2</sub>(o-phen)] than GC<sub>RDE</sub>/Nf/[Mn(aptt)(Cl)(o-phen)<sub>2</sub>]·2Haptt·H<sub>2</sub>O for ORR. The bulky moiety attached to the complex 2 may hinder the catalytic activity and subsequently decreases its ORR activity. On comparing the present studies with the literature [26-28,54-55], these complexes immobilized electrodes have significant advantages in the ORR activity. The ORR onset potential of cobalt based coordination polymer in 0.1 M KOH is 0.81 V [27]. The ORR onset potential at MWCNTs-CoTPP. MWCNTs-CoTCPP and MWCNTs-CoTHPP composites are 0.78, 0.82 and 0.81 V, respectively in 0.1 M KOH [28]. MnO based catalyst shows the ORR onset potential at 0.87 V in 0.1 M KOH [55]. Accordingly, the ORR activity at GC<sub>RDE</sub>/Nf/[Mn (ppt)<sub>2</sub>(o-phen)] and GC<sub>RDE</sub>/Nf/[Mn(aptt)(Cl)(o-phen)<sub>2</sub>]·2Haptt·H<sub>2</sub>O is comparable/superior to most of the reported ORR catalysts [27,28,55]. Thus it is demonstrated that the complexes 1 and 2 have significant ORR activity in basic medium.

#### 5. Conclusion

This paper reports on the synthesis, structural, spectral, single crystal X-ray diffraction data, photoluminescence and thermal properties of two complexes, [Mn(ppt)<sub>2</sub>(o-phen)] (1) and [Mn (aptt)(Cl)(o-phen)<sub>2</sub>]·2Haptt·H<sub>2</sub>O (2) containing o-phen as a coligand. Both the complexes are six coordinated and heteroleptic with distorted octahedral geometries around metal centre. The coordination sphere of complex 1 is fulfilled by two amide carbonyl oxygen and a deprotonated hydrazine nitrogen atom of two uni-negative bidentate ppt ligand and two nitrogen atoms of o-phen; each forming three five membered chelate rings. In complex 2, the coordination sphere of Mn(II) is fulfilled by four nitrogen atoms of two o-phen, one thiolato sulfur atom of aptt ligand and one chloride ion. The X-ray studied of complex **2** reveals that the complex with aptt ligand resulted from tautomerization of Haptt with subsequent deprotonation. The crystal structure of complexes are stabilized by various inter and intramolecular hydrogen bonding interactions. In addition, weak C–H $\cdots$  $\pi$  and  $\pi \cdots \pi$  interactions are present in complex **2** providing added stability. Photoluminescence properties of complexes show that these complexes may be used as potential photoactive materials. Thermogravimetric analysis of both complexes indicates that finally metal is converted into its metal oxide at higher temperature. The complexes 1 and 2 immobilized electrodes were prepared using GC electrode and Nafion. GC<sub>RDE</sub>/Nf/[Mn(ppt)<sub>2</sub>(o-phen)] and GC<sub>RDE</sub>/Nf/[Mn(aptt)(Cl)(o-phen)<sub>2</sub>]·2Haptt·H<sub>2</sub>O possess high catalytic activity towards ORR in 0.1 M KOH. Accordingly, complexes 1 and 2 could be used as the low-cost and efficient oxygen reduction electrocatalysts in the fuel cells, metal-air batteries and chloralkali electrolyzers.

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# Appendix A. Supplementary data

CCDC 1849178 and 1849179 contains the supplementary crystallographic data the complexes **1** and **2**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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