



Synthesis, characterization and supramolecular building motifs of substituted salphen- and thiasalphen–metal complexes



Nitesh Kumar, Ashish K. Asatkar*, Snigdha Panda, Sanjio S. Zade*

Department of Chemical Sciences, Indian Institute of Science Education and Research (IISER) Kolkata, Mohanpur 741246, India

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ABSTRACT

Two new series of substituted salphen–metal complexes and thiasalphen–metal complexes have been synthesized. The fluorine substituted salphen–metal complexes (**5**, **6** and **7**) were prepared by the coordination of ligand **4** (obtained by the reaction of 4,5-difluorosallylaldehyde with *o*-phenylenediamine) with Ni(II), Cu(II) and Zn(II) ions, respectively. The thiasalphen–metal complexes (**8**, **9** and **10**) were prepared strategically following the unique route of the *in situ* reduction of bis(*o*-formylphenyl)disulfide to mercaptobenzaldehyde then complexation with Ni(II), Cu(II) and Zn(II) ions, followed by Schiff base coupling with *o*-phenylenediamine, in a single pot. The products were characterized by elemental analysis, ESI-MS, FT-IR and ¹H/¹³C NMR spectroscopy. The structures of **4**, **5**, **6**, **9** and **10** were established by single crystal X-ray analysis. The various non-bonding interactions resulted in fascinating supramolecular building motifs. The photophysical and electrochemical properties (band gaps, HOMO–LUMO energies) of all the six complexes were studied by UV–Vis spectroscopy and cyclic voltammetry. The optical band gaps were found to be in the range 2.31–2.79 eV.

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1. Introduction

The coordination chemistry of salen/salphen based ligand systems has been explored extensively due to numerous distinctions, such as their straightforward synthesis, accessibility for large range of metal ions and the resourceful nature of the resulting metal complexes. Several structural modifications have been done on salen/salphen ligands to fine-tune their properties and achieve desirable materials. Metal-organic frameworks (MOFs) [1] prepared by appropriate substitutions on such ligand systems are very fashionable molecular architectures now-a-days, owing to their high efficiency as heterogeneous catalysts [2] and hydrogen storage materials [3]. Substitution at the benzene ring of salen/salphen by thiophene to yield thiophene-capped salen/salphen metal complexes has been used to generate conducting polymers [4]. Attachment of additional donor groups to the salen systems has been tactically used to develop homometallic lanthanide coordination polymers or heterometallic transition metal–lanthanide coordination polymers, due to their versatile applications [5]. Substitution of peripheral groups on the bridging unit and the aryl side groups has been used as a valuable toolkit to achieve desirable the cat-

alytic activities [6] and magnetic properties [7] of the salen–metal systems.

One of the structural aspects of the metal–salphen system, which distinguishes it from the metal–salen system, is that it possesses a conjugated planar system. It has become apparent that metal complexes possessing π -conjugated systems have significant importance in material science [8]. Metal–phthalocyanines have been known as tremendous semiconducting materials for p-channel organic field-effect transistors (OFET), while the substitution of electron withdrawing groups on the benzene rings converts these materials into n-channel OFET [9]. Recently, we have reported the metal complexes of a thiophene based salphen like system, which resulted in superb p-channel OFET materials [10]. Here, we have incorporated the strong electron withdrawing fluorine substituent on the salphen ligand to fine tune the energy levels and band gaps of the resulting complexes.

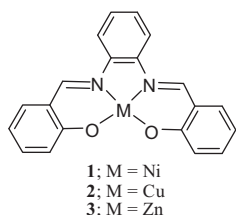
Although, salen/salphen systems are among the most studied ligand systems, their sulfur analogues are still very limited, mainly due to the instability of the thiol groups. Goswami et al. demonstrated a novel method to prepare thiosalen–Ni(II)/Cu(II)/Fe(II) complexes using the direct reaction of 2,2'-dithiodibenzaldehyde with [Ni(en)₃]²⁺/chelating thiolate donors, without any need for protection/deprotection of the thiol group [11]. Stenson et al. prepared salen/salphen–Zn(II) complexes by the reaction of 2,4-di-R-thiosallylaldehyde (R = H, ^tBu) with diamines in the presence of

* Corresponding authors.

E-mail address: ashu.asatkar@gmail.com (A.K. Asatkar).

a metal salt, while the analogous Ni(II) complexes were obtained by the transmetalation of the Zn(II) complexes with the Ni(II) ion [12]. In recent years, we also have demonstrated the synthesis of thiasalen/selenasalen systems and their metal complexes in a series of papers. We have developed bis(methyl)(thia/selena)salen ligands and explored their coordination properties towards Pd(II), Pt(II) and Ag(I) ions [13]. Recently, we developed a three-component, one pot synthesis of thiasalen/selenasalen-Ni(II), Pd(II) and Pt(II) complexes by the oxidative addition of the disulfide/diselenide bis(*o*-formylphenyl)-disulfide/-diselenide to a zero-valent metal followed by *in situ* Schiff base coupling with ethylenediamine [14]. We have also reported the synthesis of thiophene based salen and salphen type ligands, their metal complexes and the properties of the complexes [15].

Many metal-salphen systems and their properties have been reported earlier, including Ni(II), Cu(II) and Zn(II) complexes (**1**, **2** and **3**) [1–7,16]. In this paper, we report the synthesis of the new ligand **4**, as a fluorine substituted salphen system, and its Ni(II), Pd(II) and Pt(II) complexes (**5**, **6** and **7**), as well as the strategic synthesis of the thiasalphen–metal complexes (**8**, **9** and **10**) as a one-pot synthesis using the corresponding metal ions (Scheme 1). Except for complex **8**, all the other products (**4**, **5**, **6**, **7**, **9** and **10**) are reported for the first time.



2. Experimental

2.1. Materials and physical measurements

All chemicals and solvents were received from Aldrich/Merck, were of reagent grade and used without any further purification.

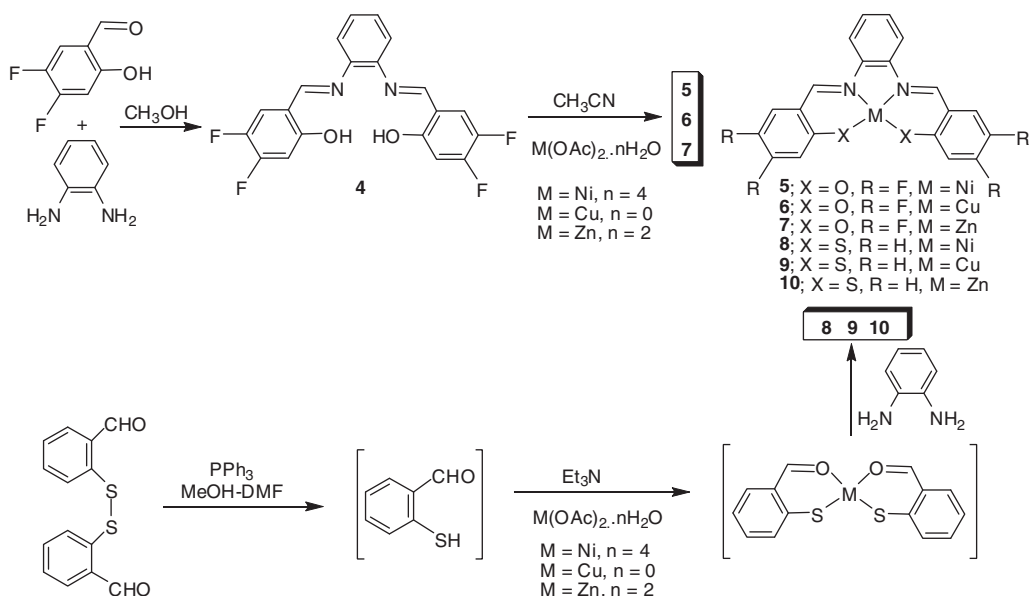
Elemental analyses were carried out on a Carlo-Erba model 1106 elemental analyzer. The mass spectra were recorded on a WATERS micromass Q-ToF micro™ instrument. Infrared spectra were recorded with KBr discs on a Perkin-Elmer spectrophotometer. NMR spectra were recorded on a JEOL-FT NMR-AL 400 MHz or a Bruker AVANCE 500 FT-NMR spectrometer using DMSO-*d*₆ as the solvent and chemical shift values are reported in ppm (δ scale) relative to Me₄Si as an internal standard. UV–Vis spectra were recorded on a Hitachi U4100 spectrophotometer, with a quartz cuvette. Cyclic voltammetry was performed with a computer-controlled Princeton Applied Research 263A electrochemical workstation using a platinum (Pt) disk as the working electrode, a Pt wire as the counter electrode and Ag/AgNO₃ (10 mM in acetonitrile) as the reference electrode. 0.1 M TBAPC was used as a supporting electrolyte.

2.2. Synthesis of ligand **4**

To a solution of *o*-phenylenediamine (170.86 mg, 1.58 mmol) in 20 mL dry methanol, 4,5-difluorosaliclaldehyde (500 mg, 3.16 mmol) was added with constant stirring under a nitrogen atmosphere. Precipitation of a pale yellow product was observed after 1 h. The precipitate was filtered off, washed with methanol and dried in vacuum. Yield: 560 mg (92%). *Anal.* Calc. for C₂₀H₁₂N₂O₂F₄: C, 61.86; H, 3.11; N, 7.21. Found: C, 61.14; H, 3.39; N, 7.68%. ESI-MS: Calc. for C₂₀H₁₂N₂O₂F₄ *m/z*: 388.0835. Found 389.0910 [M+H]⁺. FT-IR (cm⁻¹, KBr, selected): 3438, 1630, 1596, 1570, 1510, 1331, 1300, 1212, 1131, 860. ¹H NMR (400 MHz, δ , ppm, DMSO-*d*₆): 7.02–7.07 (m, 1H), 7.40–7.47 (m, 2H), 7.75–7.80 (m, 1H), 8.90 (s, 1H), 13.23 (s, 1H). ¹³C NMR (125 MHz, δ , ppm, DMSO-*d*₆): 105.78 (d, *J* = 19.25 Hz), 115.94 (d, *J* = 5.25 Hz), 118.83 (d, *J* = 16.87 Hz), 119.35, 128.09, 141.52, 142.85 (dd, *J* = 235.37 Hz, *J* = 13.62 Hz), 152.51 (dd, *J* = 251.06 Hz, *J* = 14.19 Hz), 158.45 (d, *J* = 11.12 Hz), 161.12.

2.3. General methodology for the preparation of complexes **5–7**

Ligand **4** (200 mg, 0.51 mmol) was suspended in 10 mL degassed dry acetonitrile and a degassed solution of 0.51 mmol metal acetate [Ni(OAc)₂·4H₂O (127.47 mg), Cu(OAc)₂ (93.35 mg), Zn(OAc)₂·2H₂O (112.82 mg)] in 5 mL acetonitrile was added dropwise with vigorous stirring at room temperature under a N₂ atmo-



Scheme 1. Synthesis of ligand **4** and complexes **5–10**.

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