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

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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-difluorosalicylaldehyde 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 to 2.79 eV.

Keywords: Salphen, Thiasalphen, Crystal structure, Supramolecular assemblies

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 catalysts² 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 catalytic activities⁶ and magnetic properties⁷ 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 slaphen 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-thiosalicylaldehyde $(R = H, ^{t}Bu)$ with diamines in the presence of a metal salt, while the analogous Ni(II) complexes were obtained by the transmetallation 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 disufhide/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.



Scheme 1. Synthesis of ligand 4 and complexes 5-10.

2. Experimental Section

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 microTM 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, 4,5difluorosalicylaldehyde (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 atmosphere. The reaction mixture was stirred at ambient temperature for 12 h. The precipitate formed was filtered, washed thoroughly with acetonitrile and dried in a vacuum.

5. Yield: 204 mg (88%). Anal. Calc. for $C_{20}H_{10}N_2O_2F_4Ni$: C, 53.98; H, 2.27; N, 6.30. Found: C, 53.31; H, 2.58; N, 6.02 %. ESI-MS: Calc. for $C_{20}H_{10}N_2O_2F_4Ni$ m/z: 444.0032. Found 445.0105 [M+H]⁺. FT-IR (cm⁻¹, KBr, selected): 1636, 1606, 1535, 1493, 1248, 1141, 883. ¹H NMR (400 MHz, δ , ppm, CDCl₃): 6.91-6.96 (m, 1H), 7.09-7.14 (m, 1H), 7.26-7.29 (m, 1H), 7.68-7.70 (m, 1H), 8.14 (s, 1H).

6. Yield: 220 mg (94%). Anal. Calc. for $C_{20}H_{10}N_2O_2F_4Cu$: C, 53.40; H, 2.24; N, 6.23. Found: C, 53.94; H, 2.71 N, 6.11 %. ESI-MS: Calc. for $C_{20}H_{10}N_2O_2F_4Cu$ m/z: 448.9974. Found 450.0156 [M+H]⁺. FT-IR (cm⁻¹, KBr, selected): 1612, 1542, 1495, 1370, 1245, 1141, 880.

7. Yield: 215 mg (92%). Anal. Calc. for $C_{20}H_{10}N_2O_2F_4Zn$: C, 53.18; H, 2.23; N, 6.20. Found: C, 53.94; H, 2.71 N, 6.11 %. ESI-MS: Calc. for $C_{20}H_{10}N_2O_2F_4Zn$ m/z: 449.9970. Found 451.0205 [M+H]⁺. FT-IR (cm⁻¹, KBr, selected): 1617, 1547, 1488, 1433, 1240, 1133, 873. ¹H NMR (400 MHz, δ , ppm, DMSO-*d*₆): 6.58-6.64 (m, 1H), 7.40-7.49 (m, 2H), 7.82-7.84 (m, 1H), 8.98 (s, 1H). ¹³C NMR (100 MHz, δ , ppm, DMSO-*d*₆): 109.01 (d, *J*= 10.11 Hz), 115.09 (d, *J*= 4.34 Hz), 116.56, 121.32 (d, *J*= 13.72 Hz), 127.59, 138.74, 139.60 (dd, *J*= 183.41 Hz, *J*= 11.56 Hz), 154.30 (dd, *J*= 202.19 Hz, *J*= 12.27 Hz), 161.45, 169.78 (d, *J*= 10.10 Hz).

2.4 General methodology for the preparation of complexes 8-10

To a solution of 2,2'-dithiodibenzaldehyde (400 mg, 1.45 mmol) in 20 mL degassed DMF, 20 mL degassed methanol was added under a N₂ atmosphere. Triphenylphosphine (380 mg, 1.45 mmol) was then added at a moderate rate and stirring was continued for 30 min. at room temperature. Triethylamine (390 μ l, 2.9 mmol) and the metal acetate, M(OAc)₂·nH₂O (0.5 equivalent, 0.72 mmol), were added with constant stirring. After 15 minutes of stirring, *o*-phenylenediamine (78.40 mg, 0.72 mmol) was added and the reaction mixture was stirred overnight. The precipitate that formed was filtered, washed with methanol to remove impurities and dried in a vacuum.

8. Yield: 175 mg (29%). Anal. Calc. for C₂₀H₁₄N₂S₂Ni: C, 59.29; H, 3.48; N, 6.91. Found: C, 59.01; H, 3.27; N, 6.54 %. ESI-MS: Calc. for C₂₀H₁₄N₂S₂Ni m/z: 403.9952. Found 404.1035 [M+H]⁺. FT-IR (cm⁻¹, KBr, selected): 1598, 1575, 1524, 1457, 1391, 1233, 1194, 1080, 748. ¹H NMR (400 MHz, δ, ppm, CDCl₃): 7.06 (t, 1H, J = 7.5 Hz), 7.24 (d, 1H, J = 7.0 Hz), 7.38-7.40 (m, 1H), 7.56 (d, 1H, J = 8.0 Hz), 7.79-7.81 (m, 1H), 7.82 (d, 1H, J = 8.0 Hz), 8.92 (s, 1H). ¹³C NMR (100 MHz, δ, ppm, DMSO-*d*₆): 117.65, 121.90, 128.84, 129.25, 129.50, 131.46, 137.49, 144.21, 146.47, 159.49.

9. Yield: 180 mg (30%). Anal. Calc. for C₂₀H₁₄N₂S₂Cu: C, 58.59; H, 3.44; N, 6.83. Found: C, 56.92; H, 3.03; N, 5.49 %. ESI-MS: Calc. for C₂₀H₁₄N₂S₂Cu m/z: 408.9894. Found 409.0480 [M+H]⁺. FT-IR (cm⁻¹, KBr, selected): 1603, 1575, 1528, 1455, 1396, 1186, 750.

10. Yield: 190 mg (31%). Anal. Calc. for $C_{20}H_{14}N_2S_2Zn$: C, 58.32; H, 3.43; N, 6.80. Found: C, 58.19; H, 3.33; N, 6.54 %. ESI-MS: Calc. for $C_{20}H_{14}N_2S_2Zn$: m/z 409.9890. Found

411.0558 [M+H]⁺. FT-IR (cm⁻¹, KBr, selected): 1615, 1599, 1578, 1450, 1384, 1184, 1076, 756, 739. ¹H NMR (400 MHz, δ, ppm, DMSO-*d*₆): 7.01-7.05 (m, 1H), 7.13-7.17 (m, 1H), 7.45 (d, 1H, J = 8.4 Hz), 7.49-7.53 (m, 1H), 7.62 (d, 1H, J = 8.4 Hz), 7.80-7.83 (m, 1H), 9.07 (s, 1H). ¹³C NMR (125 MHz, δ, ppm, DMSO-*d*₆):118.26, 120.96, 128.43, 130.10, 130.15, 135.94, 138.34, 140.72, 154.22, 165.84.

2.5 Crystal data collection and refinement

Suitable crystals of the compounds were collected on a SuperNova, Dual, Cu/Mo at zero, Eos diffractometer. Using Olex2,¹⁷ the structures were solved with the Superflip¹⁸ structure solution program, using Charge Flipping, and refined with the ShelXL¹⁹ refinement package using least squares minimization. The structure graphics shown in the figures were created using the Mercury software package, version 3.5. Details of the crystal parameters, data collection and refinements are listed in Table 1.

Formula	$C_{20}H_{12}N_2O_2$	$C_{20}H_{10}N_2O_2$	$C_{20}H_{10}N_2O_2$	$C_{20}H_{14}N_2S_2Cu\\$	$C_{20}H_{14}N_2S_2Zn$
	$F_4(4)$	F ₄ Ni (5)	F ₄ Cu (6)	(9)	(10)
Crystal	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
System					
Space group	<i>P</i> 2 ₁ /c	$P 2_1/n$	<i>P</i> 2 ₁ /c	$P 2_1/c$	<i>P</i> 2 ₁ /c
<i>a</i> [Å]	12.2952(4)	11.4758(13)	11.9537(4)	7.36540(10)	7.3606(2)
<i>b</i> [Å]	6.0925(2)	7.8010(4)	23.4175(10)	15.7985(3)	15.7757(6)
<i>c</i> [Å]	22.2088(6)	18.4302(16)	6.8722(2)	13.9509(3)	13.9455(4)
α [°]	90	90	90	90	90
β[°]	96.339(3)	105.945(10)	95.688(3)	94.740(2)	94.711 (2)
γ[°]	90	90	90	90	90
V[Å ³]	1653.46(9)	1586.5(2)	1914.25(12)	1617.81(5)	1613.86 (9)
Z	4	4	4	4	4
λ [Å]	0.71073	0.71073	0.71073	0.71073	0.71073
$\rho_{\rm calcd} [{\rm g cm^{-3}}]$	1.560	1.863	1.5608	1.683	1.695
<i>F</i> [000]	792	896	900	836	840
$\mu \text{ [mm}^{-1}\text{]}$	0.132	1.290	1.197	1.613	1.785
index ranges	$-16 \le h \le 15$	$-11 \le h \le 13$	$-12 \le h \le 16$	$-9 \le h \le 9$	$-8 \le h \le 9$

Table 1. Crystallographic information for complexes 4, 5, 6, 9 and 10

	$-7 \le k \le 7$	$-3 \le k \le 9$	$-31 \le k \le 30$	$-18 \le k \le 20$	$-19 \le k \le 20$
	$-29 \le l \le 16$	$-15 \le 1 \le 21$	$-9 \le l \le 8$	$-17 \le l \le 16$	$-17 \le l \le 16$
<i>T</i> [K]	100(2)	100(2)	100(2)	100(2)	100(2)
<i>R</i> 1	0.0408	0.0444	0.0603	0.0301	0.0367
wR2	0.0968	0.1064	0.2157	0.0734	0.0907
R _{merge}	0.0526	0.0510	0.2157	0.0363	0.0456
Parameters	256	262	261	226	226
GOF	1.080	1.117	0.811	1.033	1.071
reflns total	7702	4459	9617	8464	7076
unique reflns	3707	2798	5146	3470	3470
obsd reflns	3014	2486	3232	3033	2971
CCDC no.	1062850	1062851	1062852	1062853	1062854

3. Results and discussion

3.1 Characterization of ligand 4 and its complexes 5, 6 and 7

4,5-Difluorosalicylaldehyde was taken as a precursor to prepare a fluorine substituted salphen system. Ligand 4 was synthesized in excellent yield by the reaction of ophenylenediamine and 4,5-difluorosalicylaldehyde (1:2 molar ratio) in dry methanol. Elemental analysis of the product is consistent with its molecular composition. The mass spectrum of the ligand displayed a molecular ion peak at m/z 389.0910 as $[M + H]^+$. In the IR spectrum of 4, the peak at 1630 cm^{-1} is assigned to the azomethine stretching, while the broad peak at 3438 cm⁻¹ is assigned to the phenolic –OH group. The intense band at 1300 cm⁻¹ is attributed to C-O stretching. The ¹H NMR spectrum of the ligand consists of six signals, which is consistent with the proposed molecular formula. The aromatic protons of the ligand appeared as multiplets due to proton-proton coupling or proton-fluorine coupling. The resonances at 8.90 and 13.23 ppm can be assigned to the azomethine proton and phenolic proton, respectively. The ¹³C NMR spectrum of the ligand exhibits ten signals, in agreement with the proposed structure. The characteristic azomethine carbon signal appeared at 161 ppm and the two carbon atoms directly attached to the fluorine atom produced doublets of doublet at 142.85 and 152.51 ppm, respectively, as a result of carbon-fluorine coupling. Long range carbon-fluorine coupling was also observed for the carbons atoms of the difluorobenzene moiety. Reaction of ligand 4 with 1 equivalent of the metal salts

Ni(OAc)₂·4H₂O, Cu(OAc)₂ and Zn(OAc)₂·2H₂O in dry acetonitrile yielded complexes **5**, **6** and **7**, respectively. All three complexes are only poorly soluble in methanol, acetonitrile and chloroform, while complexes **6** and **7** are soluble in DMSO and DMF. The complexes are quite stable in the solid state as well as in the solution phase. Elemental analyses gave satisfactory data towards the proposed structures. Complexes **5**, **6** and **7** produced molecular ion peaks in their mass spectra at m/z 445.0105, 450.0156 and 451.0205, respectively, as the $[M + H]^+$ peak. The IR spectra of the complexes **5**, **6** and **7** displayed characteristic $v_{(C=N)}$ stretching frequencies at 1606, 1612 and 1617 cm⁻¹, respectively, which were shifted to lower wavenumbers as compared to the $v_{(C=N)}$ stretching frequency (1630 cm⁻¹) of the parent ligand **4**, suggesting the coordination of the metal ions with the ligand *via* N-donors. A strong band at around 1245 cm⁻¹ in the spectra is assigned to C-O stretching, however its significant shifting to lower frequency compared to the free ligand indicates the involvement of the O atom in coordination with the metal ions.

The NMR spectroscopic characterization of the diamagnetic complexes **5** and **7** showed the formation of symmetrical complexes. The ¹H NMR spectra of complexes **5** and **7** showed a singlet at 8.14 and 8.98 ppm, respectively, for the azomethine protons. The disappearance of the signal corresponding to the phenolic proton suggests the coordination of the phenolic oxygen atom with the metal ion in each case. The ¹³C NMR spectrum for complex **5** could not be recorded due to its poor solubility. In the ¹³C NMR spectrum of **7**, three signals at 116.56, 127.59 and 138.74 ppm are assigned to the carbon atoms of the *o*-phenylene bridge and a signal at 161.45 ppm is attributed to the azomethine group. Carbon-fluorine coupling was observed for all the six signals of the difluorobenzene moiety. The signals of the two carbon atoms attached to the fluorine atom appeared as doublets of doublet at 139.60 and 154.30 ppm.

3.2 Characterization of the thiasalphen complexes 8, 9 and 10

Treatment of the compound bis(*o*-formylphenyl)disulfide with triphenylphosphine in a 1:1 molar ratio in a DMF-methanol solvent mixture at room temperature afforded the 2-mercaptobenzaldehyde.²⁰ The complexes **8**, **9** and **10** were obtained by the *in-situ* reaction of the resulting mercaptobenzaldehyde with half equivalent of the metal salts [Ni(OAc)₂·4H₂O, Cu(OAc)₂ and Zn(OAc)₂·2H₂O], followed by the addition of half equivalent of *o*-phenylenediamine. The complexes **8-10** are poorly soluble in methanol, acetonitrile and

chloroform, whilst their solubility is good in DMSO and DMF. The complexes are found to be stable.

Elemental analyses data of the complexes are consistent with the compositions corresponding to their molecular structures. The mass spectra of complexes **8**, **9** and **10** exhibited molecular ion peaks at m/z 404.1035, 409.0480 and 411.0558, respectively, corresponding to the [M + H]⁺ peaks. In IR spectra of the complexes **8**, **9** and **10**, peaks at 1598, 1603 and 1615 cm⁻¹, respectively, are assigned to the characteristic $v_{(C=N)}$ stretching. These peaks appeared at lower energy values compared to the $v_{(C=O)}$ stretching frequency (1691cm⁻¹) of the precursor bis(*o*-formylphenyl)disulfide. A strong band at around 750 cm⁻¹ in the spectra is credited to a C-S stretching vibration. NMR spectroscopy of the diamagnetic complexes **8** and **10** revealed their symmetric nature. The azomethine protons of the complexes **8** and **10** displayed a singlet at 8.92 and 9.07 ppm, respectively, in the ¹H NMR spectra. Complexes **8** and **10** showed ten signals in the ¹³C NMR spectra for ten magnetically different types of carbon atoms. The azomethine carbon signal was observed at 159.49 and 165.84 ppm for complexes **8** and **10**, respectively. The structures of complexes **9** and **10** were confirmed by single crystal X-ray crystallography (discussed later). The structure of complex **8** has already been established as having a square planar geometry around the nickel(II) ion.²¹

3.3 Crystal structures

3.3.1 Crystal structure of ligand 4

Ligand **4** crystallized in the monoclinic space group $P2_1/c$ with one molecule in the asymmetric unit (Z = 4, Z' = 1). The crystal structure of the ligand confirmed the existence of the di(enol-imine) form. The ORTEP diagram of the ligand is shown in Fig. 1a. Both the phenolic protons are involved in intramolecular O-H...N hydrogen bonding [1.823 Å; 146.60(9)° and 1.852 Å; 147.00 (9)]. One of the two side rings is coplanar with the central benzene ring, while the other ring is rotated around the N(2)-C(14) bond to an angle of 58.12° (Fig. 1b). Thus there is no symmetry in the molecule. Selected bond lengths and bond angles are mentioned in Table 2. Weak C-H...F intermolecular interactions construct 1D tapes along the *a*-axis (Fig. 2a) while C-H...O interactions construct other 1D tapes along the *b*-axis (Fig. 2b). The overall interactions present in the molecule lead to the formation of a herringbone type network packing, as shown in Fig. 3.



Fig. 1. (a) ORTEP representation of ligand **4**; thermal ellipsoids are drawn at the 50% probability level and (b) molecular view showing twisting of **4**.



Fig. 2. 1D tapes of **4** induced *via* intermolecular C-H...F interactions along the *a*-axis (a) and C-H...O interactions along the *b*-axis (b).



Fig. 3. Packing of 4 showing the herringbone type network; view along the *bc*-plane.

	Bond lengths	Bond	angles
C1-O1	1.3419(19)	N1-C7-C6	119.67(15)
C20-O2	1.3410(19)	N2-C14-C15	120.19(14)
N1-C7	1.283(2)	N1H1-O1	146.60 (9)
N2-C14	1.282(2)	N2H12-O2	147.00 (9)
N1H1	1.823	C1-O1-H1	109.5
N2H12	1.852	С20-О2-Н12	109.5

 Table 2. Selected bond lengths (Å) and angles (°) for 4.

3.3.2 Crystal structure of complex 5

Complex 5 crystallized in the monoclinic $P2_1/c$ space group with crystallographically imposed symmetry relating to two square-planar complexes. The ORTEP diagram of the complex is shown in Fig. 4a. Complexation with the metal ion forced the ligand framework to be in a plane. The two square-planar complex units are linked through a metal-metal interaction (3.217 Å) in a centrosymmetric way. The square-planar complex units are oriented in a *trans* manner (Fig. 4b) and the crystallographic inversion center is situated at the middle of the metal-metal bond. The two Ni-O bond lengths are 1.838 and 1.837 Å, while the two Ni-N bond lengths are 1.858 and 1.862 Å. The bond lengths are consistent with those in

similar salphen systems.²² Selected bond lengths and bond angles of **5** are listed in Table 3. The π - π interactions between the dimeric units construct a pillar along the *b*-axis (Fig. 5a) and molecular packing is established by F...F and F...H interactions, leading to 1D-chains (Fig. 5b). The unit cell packing of the complex is shown in Fig. S17.



Fig. 4. ORTEP diagram of **5** (H-atoms are omitted) (a) and top view (b); drawn at the 50% probability level.



Fig. 5. 1D chains established through π - π interactions (a) and F...F interactions (b).

Bond lengths	5	6	9	10
	(M = Ni)	(M = Cu)	(M = Cu)	(M = Zn)
M1-N1	1.858(3)	1.941(4)	1.9842(17)	1.993(2)
M1-N2	1.862(3)	1.942(4)	1.9949(18)	1.984(2)
M1-O1/S1	1.838(2)	1.905(3)	2.2523(6)	2.2427(8)
M1-O2/S2	1.837(2)	1.893(4)	2.2419(6)	2.2507(8)
C1-O1/S1	1.296(4)	1.298(6)	1.738(2)	1.734(3)
C20-O2/S2	1.298(4)	1.304(6)	1.732(2)	1.739(3)
Bond angles	5	6	9	10
O1/S1-M1-O2/S2	82.79(10)	87.99(15)	84.09(2)	84.07(3)
N1-M1-N2	86.32(12)	84.24(16)	84.14(7)	84.01(10)
N1-M1-O1/S1	95.56(11)	93.58(15)	96.15(5)	96.60(7)
N2-M1-O2/S2	95.30(11)	94.33(16)	96.52(5)	96.22(7)
N2-M1-O1/S1	177.82(11)	177.13(15)	166.20(5)	176.34(7)
N1-M1-O2/S2	178.01(10)	175.17(15)	176.25(5)	165.93(7)

Table 3. Selected bond lengths (\AA) and angles $(^{\circ})$ for complexes 5, 6, 9 and 10.

3.3.3 Crystal structure of complex 6

Complex **6** crystallized in the monoclinic space group $P_{1/c}$ (Z = 4). The crystal structure of **6** displays a solvent occupancy disorder. A satisfactory model for the disordered solvent was not found, and therefore the disordered density is masked out by the 'use solvent mask' route in OLEX2. The metal center adopts a square planar geometry around the Cu(II) center. The ORTEP drawing is depicted in Fig. 6. The dihedral angle between the N1–Cu1–O1 and N2–Cu1–O2 planes is 4.82°, which indicates only a slight deviation from a square planar geometry. The Cu–O [1.905(3) and 1.893(4) Å] and Cu–N [1.941(4) and 1.942(4) Å] bond distances in **6** are comparable with those in square planar salphen-Cu(II) complexes.²³ Selected bond lengths and bond angles are listed in Table 3. The molecules form a 2D sheet *via* C-H...F and F....F intermolecular interactions (Fig. 7). π - π Interactions present between the molecules lead to cofacial packing (Fig. 8).



Fig. 6. ORTEP representation of the copper complex **6**; thermal ellipsoids are drawn at the 50% probability level.







Fig. 8. Cofacial packing of **6** established by π - π interactions.

3.3.4 Crystal structure of complex 9

Complex 9 crystallizes in the monoclinic space group $P2_1/c$. The crystal structure revealed a square planar geometry around the Cu(II) center (Fig. 9). The dihedral angle of 13.97° between the N1-Cu1-S1 and N2-Cu1-S2 planes reflects the small deviation of the coordination core from a square planar system. However, the deviation is relatively low compare to the thiasalen-Cu(II) complex.²⁴ The bond lengths of the two Cu–S bonds (2.252 and 2.242 Å) are nearly equal and the two Cu-N bond distances (1.984 and 1.995 Å) are also very close. These bond distances are very similar to those in the thiasalen-Cu(II) complex.²⁵ Selected bond lengths and bond angles are shown in Table 2. Due to the π -conjugated system in the ligand framework, strong π -stacking interactions were observed between adjacent molecules with average molecular plane distances of 3.321 and 3.328 Å (Fig. 10a). Along with the π - π interactions, Cu1...S2* (3.044 Å) interactions are also responsible for the stacking of molecular planes. The out-of-plane Cu1...S2* interactions construct a pseudodimer, where the S2-Cu1-S2* and Cu1-S2-Cu1* bond angles are 93.51 and 86.49°, respectively (Fig. 10b). However, similar out-of-plane Cu...O interactions in many Cu-salen and Cu-salphen systems have resulted in bonding to generate true dimers.²⁶ In the crystal structure of the complex, the molecules form 1-D tapes along the *c*-axis, established by C-H...S interactions (Fig. S18). Various types of non-bonding interactions present in the complex lead to the formation of 3D interlock packing (Fig. 11).



Fig. 9. ORTEP representation of complex 9; thermal ellipsoids are drawn at the 50%



Fig. 10. Spacefill view of the molecular stacking (a) and pseudo-dimer formed through Zn...S interactions (b) in **9**.

RCi



Fig. 11. Packing diagram of complex 9 showing the interlock pattern.

3.3.5 Crystal structure of complex 10

Complex 10 also crystallized in the monoclinic space group $P2_1/c$ with a square planar geometry around the Zn(II) center (Fig. 12). Kleij et al. have studied various substituted salphen-Zn(II) complexes and found their strong affinity towards dimerization through outof-plane Zn-O bonding.²⁷ A number of reports on salen-/salphen-Zn(II) complexes suggest that the Zn(II) ion strongly favours a square pyramidal geometry over a square planar geometry, and due to that the Zn(II) center can either dimerize or coordinate with solvent molecules.²⁸ Stenson et al. reported a t-butyl substituted thiasalphen-Zn(II) complex as a bridged dimer (the only reported thiasalphen-Zn(II) complex) where the coordination environment around the metal center is distorted significantly. However, the crystal structure of the parental thiasalphen-Zn(II) complex 10 revealed the existence of a monomeric unit. The dihedral angle between the N1–Zn1–S1 and N2–Zn1–S2 planes was observed to be 14.21°. The two Zn-S bonds are almost equal [2.243(8) and 2.251(8) Å] and the two Zn-N bonds are also [1.993(2) and 1.984(2) Å] virtually alike. The Zn–N and Zn–S bonds are similar to those reported for the *t*-butyl substituted thiasalphen-Zn(II) dimeric complex. Selected bond lengths and bond angles are shown in Table 3. The formation of 1-D molecular tapes due to the S...H interactions was observed along the c-axis (Fig. S19). Like complex 9, stacking (3.223 and 3.319 Å) of molecular planes induced by π - π interactions and Zn1...S*

(out of plane) interactions were observed (Fig. S20). The molecular packing of the complex is very similar to that of complex 9 (Fig. S21).



Fig. 12. ORTEP representation of complex **10**; thermal ellipsoids are drawn at the 50% probability level.

4. Photophysical properties

We recorded the absorption spectra of ligand **4** and complexes **5-10** in DMF solvent (Fig. S22). Ligand **4** displayed an intense band at 334 nm. Complexation of the ligand with Ni(II), Cu(II) and Zn(II) ions resulted in a red-shift of the strong band to 374, 412 and 394 nm, respectively. The shift is attributed to extended conjugation in the ligand framework due to its planar configuration, induced by a square planar geometry around the metal centers. Also, low intensity peaks at low energy were observed at 469 and around 429 nm (as a shoulder) for complexes **5** and **7**, respectively. The UV-visible spectrum of complex **8** consists of a very strong band at 295 nm and two low energy bands at 351 (as a shoulder) and 391 nm. In the absorption spectrum of **9** three bands were observed at 309, 338 and 474 nm. The absorption spectrum of **10** also produced three bands at 291 (as a shoulder), 334 and 427 nm. All the bands in the Ni(II) and Zn(II) complexes may be attributed to intramolecular $\pi \rightarrow \pi^*$ charge transfer bands, while those in the Cu(II) complexes may be due to intramolecular charge transfers as well as ligand to metal charge transfers. The optical band gaps, E_g^{opt} , calculated using the onset wavelength are 2.35, 2.53, 2.57, 2.79, 2.31 and 2.47 eV for complexes **5-10**, respectively.

5. Electrochemical study

Electrochemical experiments were carried out by a platinum disk electrode in a threeelectrode cell using a Pt counter electrode, Ag/AgCl reference electrode and 0.01 mM tetrabutylammonium perchlorate (TBAPC) as the supporting electrolyte in dry DMF (Fig.

13). The HOMOs of the complexes were calculated from the onset oxidation potential (E_{onset}^{ox}) of the complexes from eq 1²⁹ taking the redox potential for the ferrocene/ferrocenium couple as 4.8 eV against the Ag/AgCl electrode; $E_{1/2}$ (ferrocene) was calculated to be 0.40 V in the DMF/TBAPC solvent/electrolyte system against the Ag/AgCl reference electrode. In the anodic scan of the cyclic voltammetry (CV), the onset oxidation potentials (E_{onset}^{ox}) of complexes **5**, **6** and **7** were found to be 0.62, 0.32, 0.68 V (versus Ag/AgCl), respectively.

$$E_{\text{HOMO}} = -(E_{onset}^{ox} - E_{1/2}(\text{ferrocene}) + 4.8) \text{ (eV)}$$
(1)

The HOMO energy levels (E_{HOMO}), calculated from E_{onset}^{ox} of the complexes, are -5.02, -4.72, and -5.08 eV for **5**, **6** and **7**, respectively. The observed onset oxidation potentials (E_{onset}^{ox}) of complexes **8**, **9** and **10** are found to be 0.60, 0.34 and 0.44 V (versus Ag/AgCl), respectively, which corresponds to the HOMO energy levels of -5.00, -4.74 and -4.84 eV, respectively. The E_{onset}^{ox} and E_{HOMO} values of the complexes are listed in Table 4. In the case of the Ni(II) and Zn(II) complexes, their oxidation peaks occur at relatively higher potentials with respect to the Cu(II) complexes. Surprisingly, despite the presence of the electron withdrawing group, the HOMO energy levels of the fluorine substituted salphen-metal complexes, except for the Zn(II) complex **7**. The HOMO energy levels of complexes are analogous to that of the work function potential of the gold electrode (-5.0 eV), which may facilitate the injection of holes from a gold electrode due to a lowering in the hole-injection barrier. Thus, due to the optimum HOMO energy levels and low band gap, the complexes could be good candidates for semiconducting materials for field effect transistors.³⁰



Fig. 13. Cyclic voltammograms of complexes **5**, **6**, **7** (a) and **8**, **9**, **10** (b) (0.01 mM) in dry DMF at a scan rate of 100 mV/s.

Complexes	E ^{ox} _{onset} (V)	E _{HOMO} (eV)	λ_{onset}	E_g^{opt} (eV)	E _{LUMO} (eV)	
5	0.62	-5.02	527	2.35	-2.67	
6	0.32	-4.72	490	2.53	-2.19	Ń
7	0.68	-5.08	482	2.57	-2.51	
8	0.60	-5.00	444	2.79	-2.21	
9	0.34	-4.74	535	2.31	-2.43	
10	0.44	-4.84	502	2.47	-2.37	

Table 4. Electrochemical and photophysical properties of the complexes 5-10.

 $E_{\text{LUMO}} = E_{\text{HOMO}} + E_g^{opt}$ and $E_g^{opt} = hc/\lambda_{\text{onset}}$; hc = 1240

5. Conclusion

In summary, we have successfully synthesized two new series of salphen-metal complexes viz fluorine substituted salphen-metal complexes and thiasalphen-metal complexes. Coupling of 4,5-difluorosalicylaldehyde with o-phenylenediamine yielded the fluorine substituted salphen ligand 4 which produced complexes 5, 6 and 7 upon coordination with Ni(II), Cu(II) and Zn(II) ions, respectively. The thiasalphen-metal complexes 8, 9 and 10 were tactically synthesized following a novel route as a one-pot method by the *in situ* reduction of bis(oformylphenyl)disulfide to mercaptobenzaldehyde, followed by reactions with the metal ions [Ni(II), Cu(II) and Zn(II)] and o-phenylenediamine. Also, we believe that a large variety of metal ions can be incorporated to these ligand frameworks, following similar pathways, to develop the corresponding analogues, and the processes can be extended to develop their salen analogues as well. A crystallographic study of the complexes confirmed the square planar environment around the metal ions and revealed the existence of various non-bonding interactions resulting in interesting self-assemblies. In UV-visible spectroscopy, the intense band of the fluorine substituted salphen ligand shifted to low energy when coordinated with a metal ion, which is attributed to the enhanced conjugation in the ligand framework forced by the metal center while adopting a square planar geometry. The photophysical studies exposed an optical band gap between 2.31 to 2.79 eV. The HOMO-LUMO energy levels of all the complexes were calculated using cyclic voltammetry. The HOMO energy levels of all six complexes, possessing planar conjugated systems, are comparable to that of the gold electrode which can facilitate the injection of holes and make these complexes good semiconducting materials for field-effect transistors.

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