Chloro-Iron and Cobalt Complexes with Functionalized Quadridentate Schiff-Base Salen Ligands: Synthesis, Characterization and DFT Calculations

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Summary: New series of penta-coordinated complexes of iron (II) and cobalt(III) (**9-14**) bearing quadridentate Schif base salicylideneimine based ligands (**5-8**) were prepared and characterized by their physical properties and spectroscopic methods of analysis. The new salenes contain either chloro or methyl groups on the phenyl back bone and chloro or diethylamine on the terminal phenyl groups. The structural parameters and charge distribution as well as the influence of the electron withdrawing (EWG)/ electron releasing (ERG) substituents were evaluated via density functional theory (DFT). The data revealed that changing either the metal center or the substituents on the ligand affect the structural parameters, charge distribution, and the M-Cl bond length.

Keywords: Iron(III) complexes, cobalt(III) complexes, Tetradentate Schiff bases, DFT calculation.

Introduction

The synthesis of cyclic carbonates (CCs) has garnered significant attention during the last decades [1-7]. The coupling reaction of epoxides with carbon dioxide (CO_2) using various catalytic systems has been employed for CC synthesis. Salen complexes of different transition metals such as chromium [8, 9], cobalt [10, 11], ruthenium [12], zinc [13, 14], aluminum [15], and tin [16] have exhibited high catalytic activity in this reaction. Also, Co(III)- [10, 17-19] and Cr(III)-based complexes with multidentate Schiff bases and/or porphyrin ligands as catalytic systems for the production of both CCs and polycarbonates were reported.

Remarkably, most of the previously stated have square pyramidal geometry, with a halide ligand occupying the apical position. The applicability of the commonly used cobalt and chromium complexes may be limited due to their toxicity. Therefore, there is still a growing need for the development of safer, more effective catalytic systems that can balance energy efficiency and sustainability in the cyclic carbonate manufacturing process.

Some iron-based catalysts have been explored for the coupling reaction of epoxides and CO_2 [20-22]. Octahedral iron(II) complex with tetradentate nitrogen ligand, N, N-bis(quinolin-2-ylmethylene)-1,2-cyclohexanediamineiron(II) chloride has shown promising results for the production of cyclic propylene carbonate from propylene oxide and CO_2. The catalyst system showed fairly high yields (82–100%, at 100^{o}C and 15 bar of CO_2)] Bis(phenoxyiminato)Fe(III)-based complexes as catalysts for coupling of CO_2 with different epoxides using DMF as solvent have also been reported.

Previously, we reported on different transition metal complexes with flexible tetradentate salen ligands bearing diverse functionalities over the ligand backbone. The complexes have been used as catalyst precursors for the coupling of epoxides with CO_2. The iron(III)-based catalysts bearing electron-withdrawing substituents on the salen ligands (NEt_3, TON = 1732) showed the highest catalytic activity towards the coupling reaction of styrene oxide and CO_2 under similar reaction conditions [23]. The cost-efficiency and lower toxicity of iron complexes make them greener alternatives to toxic metal complexes used as catalyst precursors. The coupling experimental results demonstrated the impact of different functional groups on the salen ligand on the electronic properties of the metal center as well as their influence on the catalytic activity of the compounds.

In the present study, the synthesis and characterization of a new series of *penta*-coordinated iron(III) (9-12) and cobalt(III) (13-14) complexes were reported. In these compounds, the metal center is coordinated with *ortho*-phenylenebis(salicylideneimine)-based quadridentate

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Schiff base ligands [5-8] containing different electron withdrawing (EWG)/ electron releasing (ERG) substituents on both the backbone and the terminal positions. Compared to the conventional Schiff base salen ligands, these selected functionalized ligands may enable us to determine which has greater influence: the substituents present in the backbone of the ligand or those located on the axial positions. In order to elucidate the structure of the complexes and the influence of both the substituents and the metal center, Density functional theory (DFT) calculations were performed.

Experimental

Materials

Synthetic reactions were performed using Schlenk techniques. Iron(II) acetate, cobalt(II) acetate, 4,5-dimethyl-o-phenylenediamine, 4,5-dichloro-o-phenylenediamine, 5-chlorosalicylaldehyde and 4-(diethylamino)-salicylaldehyde were acquired from Aldrich. All chemicals were utilized just as supplied. Elemental analysis was carried out using HEKAtech EuroEA elemental analyzer. A Bruker Vertex 70-FT-IR spectrometer coupled with a Vertex Pt-ATR accessory was used to record the infrared spectra. A Bruker ARX300 spectrometer was utilized to record the ^{1}H- and ^{13}C-NMR spectra using $CDCl_3$ as a solvent with TMS as an internal standard. Both measurements were carried out at room temperature

Density functional theory (DFT) calculations were performed using Gaussian 09, [24] at the Becke's three-parameter hybrid exchange functional and the Lee–Yang–Parr correlation functional (B3LYP) with 6-31G(d) for H, C, N, O, Cl, and LANL2DZ basis set for Fe and Co. All structures were optimized without any geometrical constraints. All structures were optimized without any geometrical constraints in the gas phase.

Synthesis of the ligands

N,N′-4,5-dimethyl-o-phenylenebis(4-diethylaminesalicylideneimine) (**5**)

To a solution of the desired amine (**1**) (2.5 mmol) in ethanol (10.0 ml) was added drop wise a solution of 4-(diethylamino) salicylaldehyde (**3**) (1.01 g; 5.2 mmol) in the same solvent (10.0 ml). The mixture was stirred at room temperature for 3 hours, during which the color changes from colorless to yellow. After concentration of the solution, the residue was isolated, washed with ethanol (2 × 10.0 ml) and petroleum ether (3 × 10.0 ml) and dried under vacuum.

The elemental analysis for $C_{30}H_{38}N_4O_2$ (**5**); calculated: C,72.87; H, 6.59; N,13.08, found: C, 71.93; H, 7.18; N, 12.48. The color: dark brown. The yield: 1.00 g (78%). m.p: 201-203 °C. IR: (υC=N) 1620 cm^{-1}. ^{1}HNMR (δ ppm) ($CDCl_3$, 400 MHz): δ = 1.19 (t, 12H), 2.36 (s, 6H), 3.38 (q, 8H), 6.94 (m, 4H), 7.05 (d, 2H), 7.81 (m, 2H), 8.59 (s, 2H), 13.21 (s, 2H); ^{13}C-{^{1}H} NMR ($CDCl_3$, 100 MHz): δ = 162.24, 159.78, 140.07, 133.09, 132.46 128.24, 123.97, 117.33, 77.21.

N,N′-4,5-dimethyl-o-phenylenebis(5-chlorosalicylideneimine) (**6**)

To a solution of the desired amine (**1**) (3.1 mmol) in ethanol (10.0 ml) was added drop wise a solution of 5-chlorosalicylaldehyed (**4**) (1.02 g, 6.5 mmol) in the same solvent (10.0 ml). The mixture was stirred at room temperature for 3 hours, during which the color changes from colorless to yellow. After concentration of the solution, the residue was isolated, washed with ethanol (2 × 10.0 ml) and petroleum ether (3 × 10.0 ml) and dried in vacuum.

The elemental analysis for $C_{22}H_{18}N_2O_2Cl_2$ (**6**); calculated: C, 63.93; H, 4.39; N, 6.78, found: C, 63.46; H, 4.53; N, 6.74. The color: Orange. The yield: 1.21 g (92%). m.p: 233-235°C. IR (υC=N) 1614 cm^{-1}. ^{1}H NMR (δ ppm) ($CDCl_3$, 400 MHz): δ = 2.26 (s, 6H), 7.03 -7.28 (m, 6H), 7.35 (d, 2H), 8.57 (s, 2H), 13.15 (s, 2H). ^{13}C-{^{1}H} NMR ($CDCl_3$, 100 MHz): δ = 161.46, 159.84, 139.69, 137.05, 132.93, 131.10, 123.54, 120.21, 119.11.

N, N′-4,5-dichloro-o-phenylenebis(4-diethylaminesalicylideneimine) (**7**)

To a solution of the desired amine (**2**) (2.5 mmol) in ethanol (10.0 ml) was added dropwise a solution of 4-(diethylamino) salicylaldehyde (**3**) (1.01 g; 5.2 mmol) in the same solvent (10.0 ml). The mixture was stirred at room temperature for 3 hours, during which the color changes from colorless to yellow. After concentration of the solution, the residue was isolated, washed with ethanol (2 × 10.0 ml) and petroleum ether (3 × 10.0 ml) and dried in vacuum.

The elemental analysis for $C_{28}H_{32}N_4O_2Cl_2$ (**7**): calculated: C, 61.41; H, 4.72; N, 11.94; found: C, 62.6; H, 5.30; N, 10.94. The color: light-brown. The yield: 1.15 g (83%). m.p: 109-111°C; IR (υC=N) 1635 cm^{-1}. ^{1}H NMR (δ ppm) ($CDCl_3$, 400 MHz): δ = 1.12 (t, 12H), 3.38 (q, 8H), (6.98 (d, 2H), 7.02 (m, 2H), 7.37 (m, 2H). 7.41 (m, 2H), 8.59 (s, 2H), 12.77 (s, 2H).^{13}C-

{^{1}H} NMR (CDCl$_3$, 100 MHz): δ = 164.77, 161.46, 142.22, 151.47, 130.89, 108.45, 103.05, 98.15, 77.33.

N,N′-4,5-dichlor-o-phenylenebis(5-chlorosalicylideneimine) (**8**)

To a solution of the desired amine (**2**) (3.1 mmol) in ethanol (10.0 ml) was added drop wise a solution of 5-chlorosalicylaldehyed (**4**) (1.02 g, 6.5 mmol) in the same solvent (10.0 ml). The mixture was stirred at room temperature for 3 h, during which the color changes from colorless to yellow. After concentration of the solution, the residue was isolated, washed with ethanol (2 × 10.0 ml) and petroleum ether (3 × 10.0 ml) and dried in vacuum.

The elemental analysis for $C_{20}H_{12}N_2O_2Cl_4$ (**8**): calculated: C, 52.88; H, 2.66; N, 6.17; found: C, 52.81; H, 2.99; N, 6.72. The color: dark green. The yield: 1.16 g (82%). m.p: 240-243°C. IR (υC=N) 1622cm^{-1}; ^{1}H NMR (δ ppm) (CDCl$_3$, 400 MHz): δ = 6.89-7.01 (m, 4H), 7.13 (s, 2H). 7.38 (m, 2H), 8.56 (s, 2H), 12.55 (s, 2H).^{13}C-{^{1}H} NMR (CDCl$_3$, 100 MHz): δ = 163.48, 159.89, 141.55, 133.99, 131.55, 124.01, 121.15, 119.53, 119.32.

Synthesis of the complexes

Chloro(N,N′-4,5-dimethyl-o-phenylenebis(4-diethylaminesalicylidene-imine))Fe(III) (**9**)

Complex **9** was synthesized following a previously published procedure under dry nitrogen using standard Schlenk techniques

To a solution of Fe(OAc)$_2$ (0.24 g, 1.2 mmol) in methanol (20.0 ml) was added a solution of the ligand **5** (0.70g, 1.6 mmol) in toluene (10.0 ml) The mixture was refluxed for 1 hr and the then allowed to cool to give a red precipitate. The crude product was filtered, washed with methanol and dried under vacuum. A solution of *p*-toluenesulfonic acid monohydrate in CH_2Cl_2 (100 ml) was added to the isolated product with continuous stirring under dry oxygen for 3 hrs. The solvent was evaporated to dryness and the residue was washed with a mixture of CH_2Cl_2/hexane (1:3) and dried under vacuum to give the corresponding tosylate compound as dark green microcrystals. The crude product was dissolved in dichloromethane (100 ml) and washed with saturated brine solution (3x400 ml). The organic layer was collected and dried over Na_2SO_4 and concentrated. Upon addition of hexane, with vigorous stirring, a green precipitate was formed which was filtered, washed with diethyl ether and dried under vacuum.

The elemental analysis for $C_{30}H_{36}N_4O_2ClFe.2H_2O$ (**9**); calculated: C, 58.88; H, 6.59; N, 9.16; found: C, 58.18; H, 6.41; N, 8.01. Gravimetric analysis: calculated: Cl: 5.79; found: Cl: 6.21. The color: green. The yield: (0.9 g; 88%); m.p: 300-302°C. IR (υC=N) 1616 cm^{-1}.

Chloro(N, N′-4, 5-dimethyl-o-phenylenebis(5-chlorosalicylidene imine))Fe (III) (**10**)

The complex was prepared according to the previous procedure. A solution of ((5- N, N′-4,5-dimethyl-*o*-phenylenebis(5-chlorosalicylideneimine), **6** (0.35 g, 0.84 mmol) in toluene (10.0 ml) was allowed to react with Fe(OAc)$_2$ (0.15 g, 0.84 mmol) in the methanol (20.0 ml).

The elemental analysis for $C_{22}H_{16}N_2O_2Cl_3Fe.6H_2O$ (**10**): calculated: C, 43.27; H, 2.64; N, 4.58; found: C, 42.88; H, 3.20; N, 3.02. Gravimetric analysis: calculated: Cl: 17.98; found: 19.02. The color: orange. The yield: 0.15 g (15%). m.p: 290-292°C; IR (υC=N) 1649 cm^{-1};

Chloro(N,N′-4,5-dichloro-o-phenylenebis(4-diethylaminesalicyliden-eimine))Fe(III) (**11**)

The complex was prepared according to the previous procedure. A solution of *(*N,N′-4,5-dichloro-*o*-phenylenebis (4-diethylaminesalicylideneimine*)*, **7** (1.0 g, 1.8 mmol) in toluene (10.0 ml) was allowed to react with Fe(OAc)$_2$ (0.33 g,1.8 mmol) in the methanol (20.0 ml).

The elemental analysis for $C_{28}H_{30}N_4O_2Cl_3Fe.Et_2O$ (**11**): calculated: C, 55.63; H, 5.84; N, 8.11; found: C, 55.56; H, 5.64; N, 7.78. The color: black. The yield: 0.9 g (77%). m.p: 288-290°C. IR (υC=N) 1609 cm^{-1}.

Chloro(N,N′-4,5-dichlor-o-phenylenebis(5-chlorosalicylideneimine))Fe(III) (**12**)

The complex was prepared according to the previous procedure. ((N,N′-4,5-dichlor-*o*-phenylenebis(5-chlorosalicylideneimine)), **8** (0.48 g, 1.10 mmol) dissolved in toluene (10.0 ml) was added to a solution of Fe(OAc)$_2$ (0.187 g, 1.10 mmol) in the methanol (20.0 ml).

The elemental analysis for $C_{20}H_{10}N_2O_2Cl_5Fe.0.5\ Et_2O$ (**12**): calculated: C, 45.21; H, 1.85; N, 5.16; found: C, 45.2; H, 2.88; N, 4.20. The color: brown. The yield: 0.1 g (11%). m.p: 298-301°C. IR (υC=N) 1608 cm^{-1}.

Synthesis of chloro(N, N′-4, 5-dimethyl-o-phenylenebis(5-chlorosalicylideneimine)) Co(III) (**13**)

The complex was prepared according to the previous procedure used for the synthesis of the corresponding iron(III) complexes starting from ((N,N′-4,5-dimethyl-o-phenylenebis(5-chlorosalicylideneimine)), **6** (0.35 g,0.84 mmol) and Co(OAc)$_2$ (0.147 g, 0.84 mmol). The resulting precipitate was suspended in hexane, filtered off and dried under vacuum to afford a dark brown product.

The elemental analysis for $C_{22}H_{16}N_2O_2C_{l3}Co.H_2O$ (**13**): calculated: C, 50.46; H, 3.08; N, 5.35; found C, 50.1; H, 2.98; N, 4.21. The color: dark brown. The yield: 0.10 g (37%). m.p: 254-256°C. IR (υC=N) 1634cm^{-1}.

Chloro(N, N′-4, 5-dichlor-o-phenylenebis (5-chlorosalicylideneimine))Co (III) (**14**)

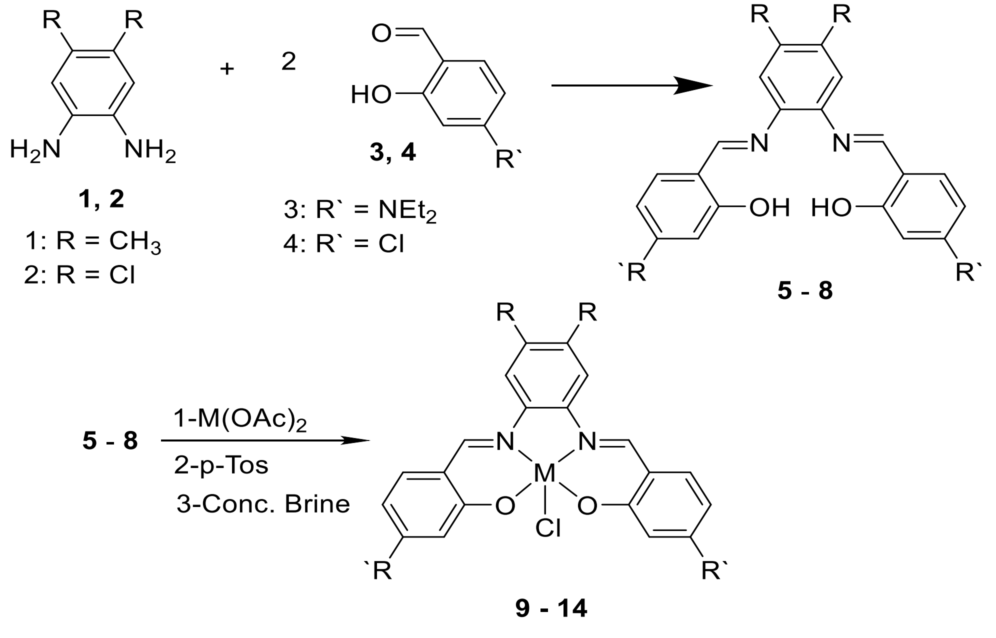
The complex was prepared according to the previous procedure. A solution of compound **8** (0.48 g, 1.1 mmol) in toluene (10.0 ml) was reacted with the Co(OAc)$_2$ (0.187 g,1.1 mmol) in the methanol (20.0 ml).

The elemental analysis for $C_{20}H_{10}N_2O_2Cl_5Co$ (**14**): calculated: C, 43.95; H, 1.83; N, 5.12; found: C, 44.81; H, 2.1; N, 3.88. Gravimetric analysis: calculated: Cl: 32.44; found: Cl: 31.76. The color: dark green. The yield: 0.1g (17.5%). m.p: 224-226°C. IR (υC=N) 1608cm^{-1};

Results and Discussion

Synthesis of the ligands

The free ligands (**5**–**8**) were efficiently synthesized by condensing the desired amines (**1** or **2**) with the corresponding aldehydes (**3** or **4**) in methanol (Fig 1). Recrystallization from a MeOH/CH$_2$Cl$_2$ (3:1 v/v) solvent mixture yielded yellow crystals of the compounds, which were characterized using physical properties, elemental analysis, IR, ^{1}H NMR, and ^{13}C NMR spectroscopy.



5, 9: M = Fe; R = CH$_3$; R` = NEt$_2$
6, 10: M = Fe; R = CH$_3$; R` = Cl
7, 11: M = Fe; R = Cl; R` = NEt$_2$
8, 12: M = Fe; R = Cl; R` = Cl
6, 13: M = Co; R = CH$_3$; R` = Cl
8, 14: M = Co; R = Cl; R` = Cl

Fig. 1: Synthetic route for the preparation of penta-coordinated iron(III) (**9**-**12**) and cobalt(III) (**13**-**14**) complexes containing *ortho*-phenylenebis(salicylideneimine)-based quadridentate Schiff base ligands.

The desired compounds (**5–8**) were confirmed through various spectroscopic techniques. The appearance of new bands between 1614 and 1635 cm^{-1} corresponding to the imine bond confirmed the formation of the salicylideneimine based ligands []25.IR spectra of the free ligands containing electron-releasing (ERG) amine groups on the terminal aromatic ring exhibited a higher frequency shift of the imine (νC=N) band (1620 cm-1 (**5**) and 1635 cm^{-1} (**7**)) compared to those with electron-withdrawing (EWG) chloro groups (1614 cm-1 (**6**) and 1622 cm-1 (**8**)).

Confirmation of the free ligands (**5–8**) was also achieved using ^{1}H NMR spectroscopy. In $CDCl_3$, singlets at approximately 8.57 ppm and 13.0 ppm were observed, corresponding to the imine proton (HC=N) and the hydroxyl proton (OH), respectively. The ^{13}C NMR spectra displayed a singlet at around 162–165 ppm, assigned to the imine (C=N) carbon [26].

Synthesis of the complexes

The iron(II) and cobalt(II) precursors, [(salen)M(II)] (M = Fe or Co) were prepared by the reaction of the salen ligand with $M(OAc)_2$ in CH_2Cl_2/MeOH (1:3) solution. The isolated compounds were then allowed to react with an equimolar ratio of *p*-toluenesulfonic acid monohydrate to afford the corresponding tosylate complexes. Substituting the tosylate ligand with Cl by extraction of the tosylate group from the compounds using brine afforded the desired penta-coordinated complexes (**9-14**, Fig. 1).

The microcrystalline complexes exhibit high hygroscopicity and air instability. The isolated Fe(III) complexes (**9-12**) and Co(III) complexes (**13** and **14**) were characterized by their physical properties, IR spectroscopy, elemental analysis, and gravimetric analysis. IR spectroscopy confirmed the reactions, as evidenced by a minor shift in the C=N stretching frequency of the ligands. Specifically, the iron complex **11** displayed a lower frequency shift of the imine (νC=N) band (1609 cm-1) compared to the corresponding ligand **7** (1635 cm^{-1}). Elemental analysis indicated a 1:1 metal to ligand ratio in the chloro complexes, suggesting a penta-coordinated arrangement around the metal center. Thermal gravimetric analysis (TGA) was performed on complexes **9**, **10** and **14**, yielding results consistent with the elemental analysis. Due to their paramagnetic behavior, NMR spectroscopy measurements were not feasible for the complexes.

DFT calculations

The optimized structures of the iron/cobalt-salen complexes (**9-14**) are shown in Fig 2, and the calculated geometrical parameters are listed in Table 1. The iron complexes (**9-12**) showed similar structure with slight variation in the bond distances and angles. For example, complex **9** with diethylamino substituents (at the lower part) showed longer Fe─Cl bond distance (2.269 Å) compared to complex **10** with chlorine substituents (2.250 Å).

Changing the substituents on the benzene diamine (upper part) from methyl groups into chlorine atoms (*e.g.* complex **9** versus **11** and **10** versus **12**) did not show a significant effect on the Fe─Cl bond distance (difference less than 0.005 Å). While changing the substituents on both the upper and lower parts showed large effect on Fe─N and Fe─O bond distances for all iron-based complexes. Single-crystal X-ray diffraction studies on comparable penta-coordinated iron(III) complexes with tetradentate O-N-N-O ligands showed Fe–O, Fe–N and Fe–Cl bond lengths almost similar to those reported in the present study. The average values are 1.888 Å (Fe–O), 2.064 Å (Fe–N), and 2.218 Å (Fe–Cl).

The structure of the cobalt-based complexes (**13** and **14**) showed similar geometrical parameters regardless of the substituents. Replacing the iron center by cobalt caused sizable reduction in the M─Cl, in which the iron complexes showed longer bond distance by 0.05 Å. Similarly, only changing the metal center caused a variation in N-M-N bond angle, with larger values for the cobalt complexes (**13** and **14**).

Table-1: Selected geometrical parameters of iron/cobalt-salen complexes (**9-14**), obtained based on the DFT-optimized structures.

	9	**10**	**11**	**12**	**13**	**14**
			Bond distance/ Å			
M-Cl	**2.269**	**2.250**	**2.264**	**2.246**	**2.210**	**2.207**
M-O1	**1.867**	**1.862**	**1.865**	**1.862**	**1.862**	**1.860**
M-O2	**1.866**	**1.864**	**1.866**	**1.862**	**1.862**	**1.860**
M-N1	**1.950**	**1.949**	**1.950**	**1.948**	**1.917**	**1.917**
M-N2	**1.950**	**1.948**	**1.950**	**1.948**	**1.917**	**1.917**
			Bond angle º			
N-M-N	**83.075**	**83.398**	**83.159**	**83.523**	**85.006**	**85.117**
O-M-O	**85.417**	**85.401**	**85.536**	**85.502**	**84.875**	**84.979**
N-M-O	**93.193**	**93.288**	**93.209**	**93.263**	**93.958**	**93.887**
N-M-Cl	**94.222** **(94.325)**	**93.798** **(93.769)**	**94.305** **(94.138)**	**93.766** **(93.700)**	**93.437** **(93.433)**	**93.371** **(93.363)**
O-M-Cl	**102.744** **(102.657)**	**102.409** **(102.408)**	**102.483** **(102.612)**	**102.183** **(102.216)**	**97.816** **(97.801)**	**97.689** **(97.697)**

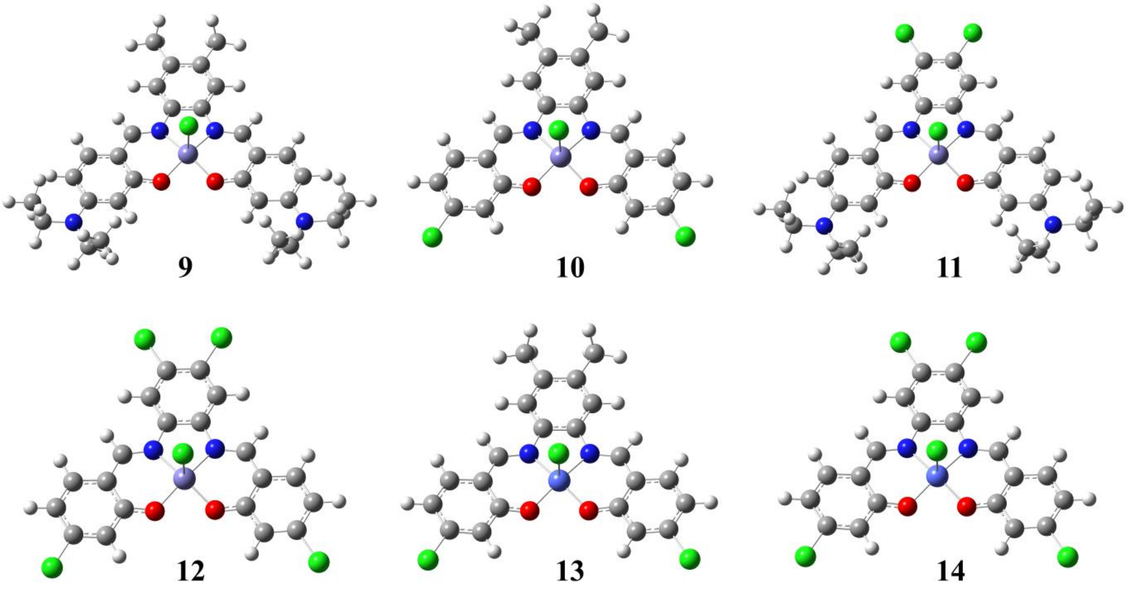


Fig. 2: DFT-optimized structures of iron/cobalt-salen complexes (**9**-**14**).

The atomic charges on selected atoms were also extracted to study the effect of electron-donating and electron-releasing groups on the charge distribution, Table-2. It can be clearly seen that the atomic charge on the metals center was not significantly affected, in which the iron complexes **9**-**12** showed very similar charge (0.568-0.576) as well as for the cobalt complexes **13**-**14** (0.455-0.458), with lower atomic charges for the cobalt complexes. In contrast, the charge on the chlorine atom which is coordinated to the metal center is reduced for chlorinated complexes compared to the ones with diethylamino groups, due the electron-releasing power of the latter. This can nicely be visualized by the calculated molecular electrostatic potential map (MESP) in Fig 3, in which the electron density on the chlorine was more negative, as indicated by the dark color for complexes **9** and **11**. Similarly, the oxygen and nitrogen atoms were more negative for complexes **9** and **11**.

Table-2: Atomic charges (Mulliken) of selected atoms iron/cobalt-salen complexes (**9**-**14**).

	9	**10**	**11**	**12**	**13**	**14**
M	**0.575**	**0.568**	**0.576**	**0.570**	**0.455**	**0.458**
Cl	**-0.311**	**-0.274**	**-0.302**	**-0.263**	**-0.216**	**-0.207**
O_1	**-0.586**	**-0.568**	**-0.584**	**-0.567**	**-0.540**	**-0.537**
O_2	**-0.586**	**-0.568**	**-0.583**	**-0.567**	**-0.540**	**-0.537**
N_1	**-0.567**	**-0.546**	**-0.571**	**-0.556**	**-0.537**	**-0.540**
N_2	**-0.568**	**-0.546**	**-0.569**	**-0.557**	**-0.537**	**-0.540**

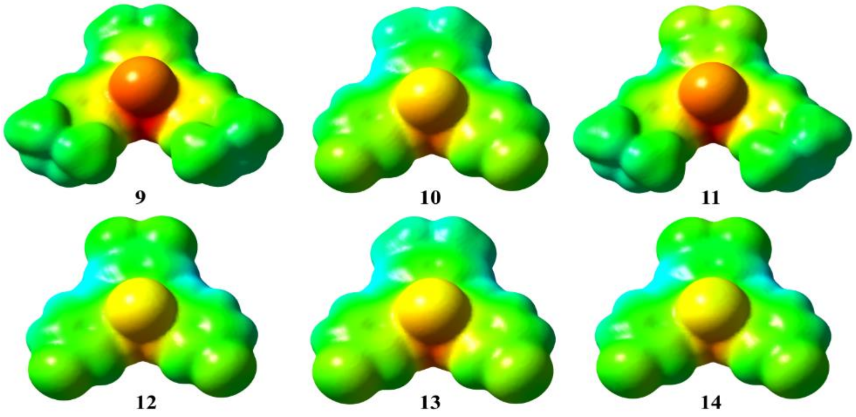


Fig. 3: Molecular electrostatic potential map (MESP) of iron/cobalt-salen complexes (blue and red colors indicate positive and negative MESP, respectively.

Conclusions

A series of new *ortho*-phenylenebis(salicylideneimine)-based quadridentate Schiff base ligands (**5**-**8**) incorporating various electron withdrawing (EWG)/ releasing substituents (ERG) on both the backbone and the axial positions were prepared. The coordination behavior of these ligands towards iron(III) and cobalt(III) was investigated. The isolated compounds were characterized by elemental analysis, IR-, ^{1}H- and ^{13}C-{^{1}H} NMR spectroscopy and gravimetric analysis. The complexes exhibited a penta-coordinated geometry. DFT calculation revealed that changing the metal center largely affect the structural parameters and charge distribution. Furthermore, it showed that having ERG substituents on the axial site of the complex led to a longer Fe-Cl bond compared with EWG groups, with less pronounced effect for the substituents in the backbone.

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