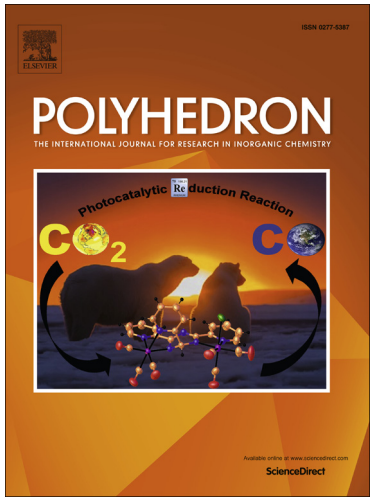

Synthesis, characterization, and X-ray crystal structure of cobalt(III) complexes with a N_2O_2-donor Schiff base and ancillary ligands. Spectral, antibacterial activity, and electrochemical studies

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Synthesis, characterization, and X-ray crystal structure of cobalt(III) complexes with a N_2O_2-donor Schiff base and ancillary ligands. Spectral, antibacterial activity, and electrochemical studies.

Mehdi Salehi[a,*], Mehdi Amirnasr[b], Soraia Meghdadi[b], Kurt Mereiter[c], Hamid R. Bijanzadeh[d], Ali Khaleghian[e]

[a]*Department of chemistry, Semnan University, Semnan, Iran*
[b]*Department of Chemistry, Isfahan University of Technology, Isfahan 84156-83111, Iran.*
[c]*Faculty of Chemistry, Vienna University of Technology, Getreidemarkt 9/164SC, A-1060 Vienna, Austria*
[d]*Department of Chemistry, Tarbiat Modarres University, Tehran, P.O. Box 14155-4838, Iran*
[e]Semnan University of Medical Science, Faculty of Medicine, Biochemistry Department, Semnan, Iran
Corresponding author:E-mail: msalehi@semnan.ac.ir (M. Salehi).

Abstract

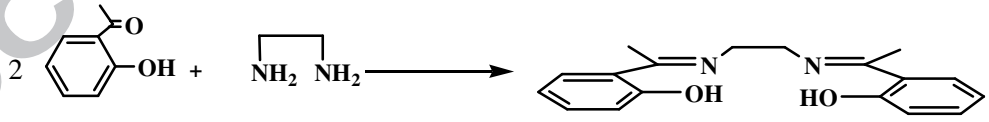
The synthesis and characterization of a series of cobalt(III) complexes of the general type *trans*-[Co(Me-salen)(L_2)]X, are described. The H_2Me-salen = *N,N'*-bis(methylsalicylidene)-1,2-ethylenediimine) and the two ancillary ligands (L) in the *trans* positions are: benzylamine (bzlan) **1**, 1-methylimidazole (1-MeIm) **2**, morpholine (mrpln) **3**, pyrolidine (prldn) **4**, 3-methylpyridine (3-Mepy) **5**, 4-methylpyridine (4-Mepy) **6**, pyridine (py) **7**. These complexes have been characterized by elemental analyses, IR, UV–Vis, and ^{1}H NMR spectroscopy. The crystal structures of *trans*-[Co^{III}(Me-salen)(bzlan)$_2$]PF_6, **1**, and *trans*-[Co^{III}(Me-salen)(3-Mepy)$_2$]PF_6, **5,** have been determined by X-ray diffraction on solvated crystals. While the Co(Me-salen) unit in **1** adopts a stepped non-planar conformation, an umbrella conformation is assumed by the Co(Me-salen) unit in complex **5**. The electrochemical reduction of these complexes at a glassy carbon electrode in acetonitrile solution indicates that the first reduction potential of Co(III/II) is irreversible, with the concomitant release of the axial ligands. Our studies showed that the metal complexes exhibit moderate antibacterial activity, and their

antibacterial activity is higher than that of the ligand against both gram positive and gram negative bacteria.

Keywords: Cobalt(III) complexes; N_2O_2 Schiff base ligand; Crystal structure, Cyclic voltammetry

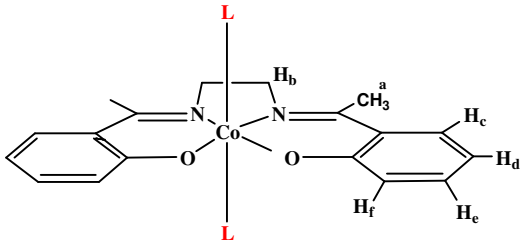
1. Introduction

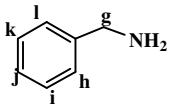
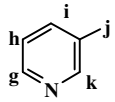
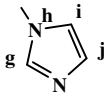
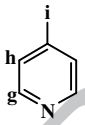
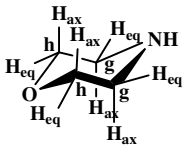
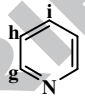
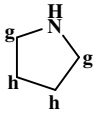
Schiff bases offer a versatile and flexible series of ligands capable of binding to the transition, non-transition, lanthanide and actinide metal ions to give complexes with suitable properties for practical applications and/or theoretical studies [1-3]. A large number of quadridentate Schiff bases and their cobalt complexes have been studied because of their interesting and important properties such as their ability to reversibly bind oxygen [4-6], their role in the elucidation of various aspects of bioinorganic chemistry [6,7-12], and their use in catalyses for oxygenation and oxidation reactions of organic compounds [13-15]. The coordination geometry of these complexes depends upon various factors including the size and electronic configuration of the central metal ions, non-bonding interactions between atoms in different ligand arms, and the inherent rigidity due to the presence of aromatic rings. The present study, is an extension to our work [16–20] with the Schiff base ligand prepared by the condensation of 2-hydroxyacetophenone with 1,2-ethylenediamine to give H_2Me-salen (Scheme 1).



Scheme 1

The synthesis and spectroscopic characterization of seven new cobalt(III) complexes (Scheme 2) and the crystal structures of two representative compounds, *trans*-[Co^{III}(Me-salen)(bzlan)$_2$]PF_6, **1**, and *trans*-[Co^{III}(Me-salen)(3-Mepy)$_2$]PF_6, **5**, are reported. The results of our cyclic voltammetry studies on these complexes are also presented and discussed.



Complex	L	Complex	L
(1)		(5)	
(2)		(6)	
(3)		(7)	
(4)			

Scheme 2

2. Experimental

2.1. *Materials and physical measurements*

All solvents and chemicals were used as received, except for the axial ligands which were distilled under reduced pressure prior to use. Elemental analyses were performed by using a Perkin-Elmer 2400II CHNS-O elemental analyzer. UV-Vis spectra were recorded on a JASCO V-570 spectrophotometer. Infrared spectra (KBr pellets) were obtained on a FT-IR JASCO 680 plus spectrophotometer. ^{1}H-NMR spectra were obtained on a BRUKER AVANCE DR X500 (500 MHz) spectrometer. Proton chemical shift are reported in part per million (ppm) relative to an internal standard of Me_4Si. The redox properties of the complexes were studied by cyclic voltammetry. Cyclic voltammograms were recorded by using a SAMA Research Analyzer M-500. Three electrodes were utilized in this system, a glassy carbon working electrode, a platinum disk auxiliary electrode and Ag wire as reference electrode. The glassy carbon working electrode was manually cleaned with 1 μm alumina polish prior to each scan. Tetrabutylammonium hexafluorophosphate (TBAH) was used as supporting electrolyte. Acetonitrile was dried over CaH_2. The solutions were deoxygenated by purging

with Ar for 5 min. All electrochemical potentials were calibrated against ferrocene-ferrocenium couple under the same conditions [21].

2.2. *Synthesis of the ligand*

H_2Me-salen, *N, N′*-bis(methylsalicylidene)-1,2-ethylenediamine, was prepared as reported in the literature [22] by the condensation of 1,2-ethylenediamine with 2-hydroxyacetophenone (1:2 molar ratio) in methanol at room temperature (Scheme 1), and was recrystallized from hot methanol. Yield: 80%. FT-IR (KBr, cm^{-1}): ν_{max} 3383–3483 (m, br, OH), 1610 (s, C=N). UV–Vis: λ_{max} (nm) (ε, L mol^{-1} cm^{-1}) (CH_3CN): 380 (960), 318 (7248), 252 (16600).

2.3. General procedure for the synthesis of complexes

The complexes shown in Scheme 1 were synthesized as follows. To a stirring solution of $Co(CH_3COO)_2{\cdot}4H_2O$ (0.125 g, 0.5 mmol) in methanol (25 ml) was added an equimolar amount of H_2Me-salen (0.148 g, 0.5 mmol). The pink solution turned red immediately upon formation the of [Co^{II}(Me-salen)] complex. The appropriate axial ligand (4 mmol) was then added to this solution, and air was bubbled through the reaction mixture for about 3 h. To the resulting dark red solution was then added 0.5 mmol of NH_4PF_6 or $NaClO_4$ and the mixture was stirred for additional 5 minutes. The products were obtained as dark red microcrystalline solids by slow evaporation of methanol at room temperature.

trans-[Co(Me-salen)(bzlan)$_2$]PF_6 ***1***: Recrystallization solvent: chloroform-propanol (2/1 v/v). Yield: 70%. Anal. Calcd for $C_{32}H_{36}CoF_6N_4O_2P$ (%): C, 53.94; H, 5.09; N, 7.86. Found (%): C, 54.00; H, 5.20; N, 7.70. FT-IR (KBr, cm^{-1}): ν_{max} 3317-3261 (m, N-H), 1599 (s, C=N), 833 (s, PF6). UV–Vis: λ_{max} (nm) (ε, L mol^{-1} cm^{-1}) (CH_3CN): 535 (356) 381 (10883), 255 (87678).

trans-[Co(Me-salen)(1-MeIm)$_2$]PF_6 ***2*****:** Recrystallization solvent: methanol. Yield: 85%. Anal. Calcd for $C_{26}H_{30}CoF_6N_6O_2P$ (%): C, 47.14; H, 4.56; N, 12.68. Found: C, 47.05; H,

4.51; N, 12.57. FT-IR (KBr, cm^{-1}): ν_{max} 1593 (s, C=N), 839 (s, PF6). UV–Vis: λ_{max} (nm) (ε, L mol^{-1} cm^{-1}) (CH_3CN): 507 (452), 380(7310), 260 (60885).

trans-[Co(Me-salen)(mrpln)$_2$]ClO_4 ***3***: Recrystallization solvent: methanol. Yield: 80%. Anal. Calcd for $C_{26}H_{36}ClCoN_4O_8$ (%): C, 49.81; H, 5.79; N, 8.94. Found (%): C, 49.00; H, 6.00; N, 8.40. FT-IR (KBr, cm^{-1}): ν_{max} 3208 (m, N-H), 1597-1585 (s, C=N), 1085 (s, ClO_4). UV–Vis: λ_{max} (nm) (ε, L mol^{-1} cm^{-1}) (CH_3CN): 555 (284), 383 (7301), 257 (46359).

trans-[Co(Me-salen)(prldn)$_2$]ClO_4 ***4***: Recrystallization solvent: methanol. Yield: 55%. Anal. Calcd for $C_{26}H_{36}ClCoN_4O_6$ (%): C, 52.49; H, 6.10; N, 9.42. Found (%): C, 52.40; H, 6.30; N, 9.50. FT-IR (KBr, cm^{-1}): ν_{max} 3245 (m, N-H), 1590 (s, C=N), 1094 (s, ClO_4). UV–Vis: λ_{max} (nm) (ε, L mol^{-1} cm^{-1}) (CH_3CN): 540 (288), 388 (9221), 255 (68167).

trans-[Co(Me-salen)(3-Mepy)$_2$]PF_6 ***5***: Recrystallization solvent: methanol. Yield: 65%. Anal. Calcd for $C_{30}H_{32}CoF_6N_4O_2P$ (%): C, 52.64; H, 4.71; N, 8.19. Found (%): C, 52.38; H, 4.65; N, 8.12. FT-IR (KBr, cm^{-1}): ν_{max} 1591 (s, C=N), 839 (s, PF_6). UV–Vis: λ_{max} (nm) (ε, L mol^{-1} cm^{-1}) (CH_3CN): 527(351), 375(8467), 255(46642).

trans-[Co(Me-salen)(4-Mepy)$_2$]PF_6 ***6***: Recrystallization solvent: methanol. Yield: 55%. Anal. Calcd for $C_{30}H_{32}CoF_6N_4O_2P$ (%): C, 52.64; H, 4.71; N, 8.19. Found (%): C, 52.61; H, 4.74; N, 8.15. FT-IR (KBr, cm^{-1}): ν_{max} 1590 (s, C=N), 839 (s, PF_6). UV–Vis: λ_{max} (nm) (ε, L mol^{-1} cm^{-1}) (CH_3CN): 524(401), 376 (7833), 253 (50532).

trans-[Co(Me-salen)(py)$_2$]ClO_4 ***7***: Recrystallization solvent: methanol. Yield: 60%. Anal. Calcd for $C_{28}H_{28}ClCoN_4O_6$ (%): C, 55.05; H, 4.62; N, 9.17. Found (%): C, 54.83; H, 4.56; N, 9.13. FT-IR (KBr, cm^{-1}): ν_{max} 1590 (s, C=N), 1092 (s, ClO_4). UV–Vis: λ_{max} (nm) (ε, L mol^{-1} cm^{-1}) (CH_3CN): 530 (339), 376 (6235), 259 (52383).

2.4. *Crystal structure determination*

For X-ray data collection red crystals of **1** in the form of the solvate, **1**·$CHCl_3$, and dark red crystals of **5** in the form of the disordered methanol solvate, **5**·*solv*, were obtained by slow

evaporation of a chloroform/1-propanol (1/1 v/v) and methanol solution of the respective complexes. X-ray data were collected on a Bruker Smart APEX CCD diffractometer with graphite monochromated Mo Kα (λ = 0.71073 Å) radiation. Full spheres of reciprocal lattice were scanned by 0.3° steps in omega with a crystal–to–detector distance of 5 cm. Cell refinement and data reduction were performed with the help of the SAINT program [23]. Corrections for absorption was carried out with the multi-scan method and program SADABS [23]. The structures were solved with direct methods using SHELXS97 and structure refinement on F^2 was carried out with SHELXL97 program [24]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were inserted in idealized positions and refined riding with the atoms to which they were bonded. For **1** a modest disorder of the $CHCl_3$ molecule was taken into account. In the case of **5** the PF_6 group was disordered (two alternative orientations in 0.769(5) / 0.231(5) proportion) and the solvent (CH_3OH) as well. In this case the solvent was squeezed with program PLATON [25]. The crystallographic and refinement data are summarized in **Table 1**.

Table 1. Crystal data and structure refinement for **1** and **5.**

Empirical formula	$C_{33}H_{37}Cl_3CoF_6N_4O_2P$ (**1**·$CHCl_3$)	$C_{30}H_{32}CoF_6N_4O_2P$ (**5**·*solv*)[a]
Formula weight	831.92	684.50
Temperature(K)	100(2)	100(2)
Radiation, wavelength	Mo Kα, 0.71073	Mo Kα, 0.71073
Crystal system, space group	monoclinic, $P2_1/n$	Monoclinic, $P2_1/c$
a (Å)	10.9608(6)	15.4352(8)
b (Å)	25.1354(13)	12.9444(7)
c (Å)	13.3639(7)	17.3965(10)
β (°)	104.532(1)	113.173(1)
Volume (Å^3)	3564.0(3)	3195.4(3)
Z	4	4
D_{calc} (g cm^{-3})	1.550	1.428
Crystal colour and size (mm^3)	red, 0.60 × 0.40 × 0.30	dark red 0.60 × 0.53 × 0.30
μ (mm^{-1})	0.804	0.656
F (000)	1704	1408
θ Range (°)	2.26 - 30.02	2.55 - 30.10
Index range	$-15 \le h \le 15$ $-35 \le k \le 35$	$-21 \le h \le 21$ $-18 \le k \le 18$

	$-18 \le l \le 18$	$-24 \le l \le 24$
Reflection collected	46733	45615
Independent reflections	10347 [R_{int} = 0.0285]	9390[R_{int} = 0.0218]
Reflections with $F^2>2\sigma$	8656	8279
Absorption correction	multi-scan	multi-scan
Max. and min. transmission	0.78 and 0.63	0.82 and 0.67
Data/ restraints/ parameters	10347/ 0/ 467	9390/ 342/ 425
Goodness-of-fit on F^2	1.087	1.092
Final R indices [$F^2 > 2\sigma(F^2)$]	R_1 = 0.0418, wR_2 = 0.0961	R_1 = 0.0355, wR_2 = 0.0950
R indices (all data)	R_1 = 0.0542, wR_2 = 0.1030	R_1 = 0.0416, wR_2 = 0.0989
Largest difference peak, hole (e Å^{-3})	0.95 and -0.88	0.73 and -0.88

2.5 Biological studies

2.5.1. Bacterial strains.

Metal complexes and ligands were individually tested against a penal of microorganisms (Gram negative and Gram positive), namely *Bacillus subtilis* (*B. subtilis*; Gram positive, ATCC 6633); *Staphylococcusaureus* (*S.aureus*; Gram positive, ATCC 25923), *Salmonella Typhi* (*S*. Typhi; Gram negative, ATCC 19430) and *Escherichiacoli* (*E.coli*;Gram negative, ATCC 25922), The organisms were purchased from Iranian Research Organization for Science and Technology (IROST).

2.5.2. Minimum inhibitory concentrations (MICs)

In vitro antibacterial activities of the complexes of the chemicals were carried out by the broth twofold dilution method as a quantitative assay [26]. Briefly, serial diluted chemical compounds in the range of 1- 6.2 µg/mL were added to a final inoculum of approximately 1.5×10^6 organisms per mL in log-phase growth. The cultures were incubated on a rotary shaker at 37°C for 24 h. Minimum inhibition concentration MIC (µg/mL) which is defined as the lowest concentration of the sample which inhibits bacterial growth was determined in sterile plates compared to the drug-free control wells. All the tests were performed in duplicates on different days to measure the reproducibility of the tests.

2.5.3 Minimal bactericidal concentration (MBC)

To measure the minimal bactericidal concentration (MBC), 100 µL volumes of all clear (no growth) tubes from a dilution MIC test was spread on to separate agar plates and incubated at 37 °C for 24 h. For determination of the MBC (mg/ml) as the lowest concentration that did not grow on nutrient agar plate [27].

2.5.4 Disc diffusion assay.

Antibacterial activity of the ligands and metal complexes were carried out using the disc diffusion method as a qualitative assay, described by Bauer et al. [28]. Four to five colonies of each organism were inoculated into 4 mL of broth and incubated for 4-6 h at 37° C. Bacterial suspension's turbidity was compared and equalized with the Mac Farland 0.5 standard [29]. Bacteria were cultured on agar plates using sterile absorbent cotton swabs. Each organism was tested in duplicate on different days to measure the reproducibility of the test. Kanamycine (10 µg per disc) and Chloramphenicol (10 µg per disc), purchased from Padtan Teb Company (Iran), were used as reference antibacterial agents. A set of assay tubes containing only inoculated medium was kept as negative control and likewise solvent controls were also done simultaneously. All assays were performed in duplicate.

3. Result and discussion

3.1. Synthesis

All cobalt(III) complexes were prepared by the direct reaction of the corresponding ligand, H_2Me-salen, and $Co(CH_3COO)_2{\cdot}4H_2O$ in the presence of the appropriate axial ligand under aerobic conditions (Scheme 2). In the preparation of complexes (**1-7**), a vigorous stream of air was passed through a solution of Co^{II}(Me-salen) in methanol to which was gradually added excess ancillary ligand. The air oxidation was continued for a period of 3 h, during which the color changed from red to red brown. Red to dark red crystals of these complexes was obtained in good yield (50-85%).

3.2. ***Spectroscopic studies***

The structures were identified by infrared, UV–Visible, Elemental Analyses, and ^{1}H-NMR spectra (Table 2 and Table 3). A comparative study of the FT-IR spectral data of the reported complexes with those of the uncomplexed ligands gives meaningful information regarding the bonding sites of the ligand molecules. H_2Me-salen shows a broad band characteristic of the OH group in the 3383-3483 cm^{-1} regions. The absence of this band in the FT-IR spectra of the complexes is indicative of the fact that the tetradentate ligand is coordinated as a dianion. The ν(C=N) band appearing at 1610 cm^{-1} in H_2Me-salen is shifted to lower frequencies by 11–25 cm^{-1} in the corresponding cobalt complexes, indicating a decrease in the C=N bond order due to the coordination of the imine nitrogen to the metal and back bonding from the Co(III) metal to the π* orbital of azomethine group [18].

The ^{1}H-NMR spectral measurements were performed in $CDCl_3$ solution. The main parameters of ^{1}H-NMR spectroscopic data of seven cobalt complexes are given in the **Table 3**. The observed signals in Me-salen ligand at 3.99 (singlet), 2.39 (singlet) and 6.5–7.52 ppm are assigned to aliphatic protons of the ethylene chelate ring, the two CH_3 groups on Me-salen and the aromatic protons of the phenyl rings of the equatorial ligand, respectively. The signal appearing as a singlet at 3.94–4.45 ppm in the ^{1}H NMR spectrum of these complexes is assigned to the two CH_3 groups on Me-salen and indicates that the equatorial coordination sites are occupied by Me-salen ligand leading to the magnetically equivalent CH_3 protons. The signals due to the aliphatic protons of the ethylene chelate ring appear at δ = 2.80–2.96 ppm. The aromatic protons of the phenyl rings in the coordinated Schiff base ligand appear in the appropriate region at 6.49-7.7 ppm.

The electronic absorption spectrum of H_2Me-salen in acetonitrile consists of two relatively intense bands centered at 252 and 318 nm, assigned to the π→π* transitions of the benzene ring of salicylaldehyde and the azomethine group respectively. A third band at 380 nm, corresponding to n→π*, disappears from the UV-Vis spectra of the cobalt complexes upon

coordination of the ligand [30, 31]. The intraligand π→π* transition of the azomethine group is red shifted by about 70 nm in the corresponding cobalt complexes and appears in the range of 375 to 388 nm [32]. The first d→d transition in different Me-salen cobalt complexes (**1-7**) appears as a shoulder in the range of 510 to 555 nm (ε = 283-434). This transition is well correlated with the basicity of the axial ligands and the reduction potentials of the corresponding Co(III) complexes.

Table 2. FT-IR, analytical data and UV-Vis for complexes.

Complex	Selected IR[a] $\upsilon_{(C=N)}$, $\upsilon_{(P-F)}$ or $\upsilon_{(Cl-O)}$	Elemental analysis Anal.Calc. (Found)	UV-Vis: λ_{max} (nm) (ε, M^{-1} cm^{-1})[b]
1	1599, 833	C: 53.94 (54.00); H: 5.09 (5.20); N: 7.86 (7.70)	535 (356), 381 (10883), 255 (87678)
2	1593, 839	C: 47.14 (47.05); H: 4.56 (4.51); N: 12.68 (12.57)	507 (452), 380(7310), 260 (60885)
3	1597-1585, 1085	C: 49.81 (49.00); H: 5.79 (6.00); N: 8.94 (8.40)	555 (284), 383 (7301), 257 (46359)
4	1590, 1094	C: 52.49 (52.40); H: 6.10 (6.30); N: 9.42 (9.50)	540 (288), 388 (9221), 255 (68167)
5	1591, 839	C: 52.64 (52.38); H: 4.71 (4.65); N: 8.19 (8.12)	527(351), 375(8467), 255(46642)
6	1590, 839	C: 52.64 (52.61); H: 4.71 (4.74); N: 8.19 (8.15)	524(401), 376 (7833), 253 (50532)
7	1590, 1092	C: 55.05 (54.83); H: 4.62 (4.56); N: 9.17 (9.13)	530 (339), 376 (6235), 259 (52383)

[a]KBr pellets, [b]Solvent is acetonitrile.

Table 3. ^{1}HNMR data for *trans*-[Co^{III}(Me-salen)$(L)_2$)]X at 298 K.

L	H_a	H_b	H_d	H_f	H_e	H_c	Other peaks
Bzlan (**1**)	2.75 (br s) (6H)	3.94 (br s) (4H)	6.70 (m) (2H)		6.86 (br dd) (4H,$H_{e,f}$)	7.70 (br d) (2H)	3.23 (m, 4H, H_g) 7.20 (m, 6H, $H_{l,h,j}$) 7.33 (m,4H, $H_{i,k}$) 2.73 (br s, 4H)
1-MeIm (**2**)	2.80 (br s) (6H)	4.10 (br s) (4H)			6.52-7.47 (14H,$H_{c,d,e,f,g,i,j}$) 3.57 (br s, 6H, H_h)		
Mrpln (**3**)	2.96 (br s) (6H)	4.45 (brs) (4H)	6.70 (br t) (2H)	7.39 (br d) (2H)	7.32 (br t) (2H)	7.65 (br d) (2H)	2.12 (br m, 4H, $H_{g,ax}$) 2.27 (br d, 4H, $H_{g,eq}$) 3.25 (m, 4H, $H_{h,ax}$) 3.48 (br dd, 4H, $H_{h,eq}$) 2.54 (br t, 2H)
Prldn (**4**)	2.87 (br s) (6H)	4.27 (s) (4H)	6.63 (br t) (2H)	7.36 (br) (2H)	7.27 (br m) (2H)	7.59 (br d) (2H)	1,48 (br s, 8H, H_h) 1.95, 2.32 (br m, 8H, H_g)

							3.01 (m, 2H,)
3-Mepy (**5**)	2.84 (br s) (6H)	4.17 (br s) (4H)	6.49 (br t) (2H)	7.28 (br d) (2H)	7.14 (br td) 2H)	7.38 (br dd) (2H)	2.18 (br s, 6H, H_j) 7.10 (br t, 2H, H_h) 7.40 (br d, 2H, H_i) 7.88 (br d, 2H, H_g) 8.01 (s, 2H, H_k)
4-Mepy (**6**)	2.82 (br s) (6H)	4.15 (br s) (4H)	6.50 (br t) (2H)	7.28 (br m) (2H)	7.15 (br t) (2H)	7.38 (br dd) (2H)	2.28 (br s, 6H, H_i) 7.00 (br d, 4H, H_h) 7.95 (br d, 4H, H_g)
Py (**7**)	2.87 (br s) (6H)	4.25 (br s) (4H)	6.50 (br d) (2H)	7.29 (br dd) (2H)	7.16 (br td) (2H)	7.38 (br dd) (2H)	7.63 (br t, 2H, H_i) 8.22 (br d, 4H, H_g) 7.23 (br t, 4H, H_h)
Me-salen	2.39 (s) (6H)	3.99 (br s) 4H)	6.79 (br td) (2H)	6.93 (br d) (2H)	7.28 (br td) (2H)	7.52 (br dd) (2H)	15.80 (br s) (2H)

3.3. *Crystal structures of complexes (1) and (5)*

3.3. 1. Trans-[Co^{III}(Me-salen)(bzlan)$_2$]PF_6 (1)

The structure of complex **1** consists of a mononuclear cobalt(III) unit, depicted in **Fig 1**. Selected bond lengths and angles are given in **Table 4**.

Table 4. Selected bond lengths [Å] and angles [°] for **1** and **5**.

1		**5**	
Bond lengths			
Co1-O1	1.8782(13)	Co1-O1	1.8867(11)
Co1-O2	1.8783(13)	Co1-O2	1.8858(11)
Co1-N1	1.8992(15)	Co1-N1	1.8968(14)
Co1-N2	1.9051(15)	Co1-N2	1.8927(14)
Co1-N3	1.9762(15)	Co1-N3	1.9529(14)
Co1-N4	1.9751(15)	Co1-N4	1.9735(14)
Bond angles			
O1-Co1-O2	85.48(6)	O2-Co1-O1	89.88(5)
O1-Co1-N1	93.48(6)	O1-Co1-N1	91.43(5)
O2-Co1-N1	178.75(6)	O2-Co1-N1	178.55(6)
O1-Co1-N2	178.40(7)	O1-Co1-N2	176.15(6)
O2-Co1-N2	93.80(6)	O2-Co1-N2	92.82(5)
N1-Co1-N2	87.25(7)	N2-Co1-N1	85.91(6)
O1-Co1-N4	85.71(7)	O1-Co1-N4	86.55(5)
O2-Co1-N4	86.81(6)	O2-Co1-N4	88.65(6)

N1-Co1-N4	93.82(6)	N1-Co1-N4	92.05(6)
N2-Co1-N4	92.82(7)	N2-Co1-N4	90.76(6)
O1-Co1-N3	88.17(6)	O1-Co1-N3	90.95(5)
O2-Co1-N3	88.09(6)	O2-Co1-N3	88.84(5)
N1-Co1-N3	91.18(6)	N1-Co1-N3	90.51(6)
N2-Co1-N3	93.24(6)	N2-Co1-N3	91.85(6)
N4-Co1-N3	172.32(7)	N3-Co1-N4	176.46(6)

The Me-Salen ligand shows a transoid conformation in complex **1**. The average values of the Co–O and Co-N bond lengths in the equatorial ligand plane are 1.8783(13) and 1.9022(15) Å, respectively. The distances between the cobalt atom and the two axial nitrogen donor atoms differ only slightly (1.9762(15) and 1.9751(15) Å) and compare well with the Co–N distances found in cobalt-ammine complexes, e.g. $[Co(NH_3)_6]Cl_3$ (Co–N = 1.963 Å) and [Co(3-Cl-acacen)$(NH_3)_2$]BPh_4 (Co–N = 1.955 Å) [33, 7]. The Co–N_{eq} is shorter than Co–N_{ax} by about 0.073 Å in complex **1** due to the presence of π-backbonding in Co–N_{imine} of the equatorial ligand. The difference is 0.069 Å in [Co(3-Cl-acacen)$(NH_3)_2$]BPh_4 (Co–N = 1.955 Å). The solid state compound contains a $CHCl_3$ molecule which shows a moderate underoccupancy and subordinate disorder (two solvent peaks near Cl(3)). The two NH_2 groups show weak hydrogen bonding, for each one NH_2 group only one H is hydrogen bonded with a nearby PF_6 octahedron (**Table 5**), while each second hydrogen exhibits no significant H-bond interaction. There is also some C-H---F interactions, which are not included in the H-bond compilation. One of these C-H---F interactions is between the $CHCl_3$ carbon C(1s) and F(1).

Table 5. Hydrogen bonds for *trans*-Co^{III}(Me-salen)(bzlan)$_2$]PF_6 (**1**·$CHCl_3$).

D-H···A	d(D-H) (Å)	d(H···A) (Å)	d(D···A) (Å)	<(DHA) (°)
N3-H3B...F3[a]	0.92	2.27	3.189(2)	174
N4-H4B...F6	0.92	2.49	3.374(2)	160
C9-H9A...F4	0.99	2.49	3.218(3)	130
C9-H9B...F2[a]	0.99	2.41	3.226(3)	139
C19-H19A...O2	0.99	2.58	3.098(3)	113
C21-H21...F1[a]	0.95	2.54	3.373(3)	147
C26-H26A...O1	0.99	2.56	3.068(3)	112

Symmetry transformation used to generate equivalent atoms:
a= -1/2+x,1/2-y,-1/2+z

3.3. *2. Trans-[Co^{III}(Me-salen)(3-Mepy)$_2$]PF_6 (5)*

As described in the experimental section, the solid state form of complex **5** was a disordered solvate **5**·*solv* with an unknown solvent content obtained from methanol. The structure contains a mononuclear cobalt(III) unit, depicted in **Fig 2.** Selected bond lengths and angles are given in **Table 4**. The Me-salen ligand shows a cisoid conformation in complex **5**. There are two 3-methylpyridine molecules attached to the metal atom to fill its axial sites with a perpendicular disposition. The two phenolic oxygen atoms and the two imine nitrogen atoms are located in *cis* positions. The average Co–N_{eq} distance (1.8948 Å) is considerably longer than that of $[Co(salen)(py)_2]BPh_4$ (1.888 Å) and shorter than that of $[Co^{III}(Me\text{-}salpn)(py)_2]PF_6$ (1.963 Å) [20]. The N(1)–Co–N(2) angle (85.91(6)˚) is smaller than the corresponding angle in the related $[Co^{III}(Me\text{-}salpn)(py)_2]PF_6$ complex (95.69(7)˚) and slightly larger than in the related salen complex (85.5(2)˚) [34].

3.4. Electrochemical studies

The cyclic voltammetric studies of *trans*-$[Co(Me\text{-}salen)(L)_2]X$ complexes (**1-7**) were conducted at 25 ˚C under an argon atmosphere using acetonitrile solutions containing 0.1 mol dm^{-3} TBAH as supporting electrolyte and complex concentrations of about 4×10^{-3} mol dm^{-3}. The reduction potential data of cobalt complexes are summarized in **Table 6**.

Table 6. Redox potentials of cobalt complexes of Me-salen in acetonitrile at 298 K.

Complex	E_{pc1}	E_{pa1}	E_{pc2}	pK_b
$[Co^{III}(Me\text{-}salen)(bzlan)_2]PF_6$ (with excess bzlan)	– 0.791	–0.629	–1.468	5.18[35]
$[Co^{III}(Me\text{-}salen)(bzlan)_2]PF_6$	–0.791	–0.073	–1.468	5.18
$[Co^{III}(Me\text{-}salen)(py)_2]ClO_4$	–0.549	0.001	–1.470	8.77[36]
$[Co^{III}(Me\text{-}salen)(mrpln)_2]ClO_4$	–0.551	–0.004	–1.467	5.51[35]
$[Co^{III}(Me\text{-}salen)(prldn)_2]ClO_4$	–0.723	–0.147	–1.472	2.69[35]
$[Co(Me\text{-}salen)(3\text{-}Mepy)_2]PF_6$	–0.580	0.118	–1.466	8.3[36]
$[Co^{III}(Me\text{-}salen)(4\text{-}Mepy)_2]PF_6$	–0.606	–0.013	–1.466	8.01[36]
$[Co^{III}(Me\text{-}salen)(MeIm)_2]PF_6$	–0.848	–0.087	–1.472	7.05[37]

The ligand is electro-inactive over the range of +0.7 to –1.8 V. The cyclic voltammogrm of **1** is presented in **Fig 3**. The first irreversible reduction at the -0.791 V is attributed to the following reaction:

$$trans\text{-}[Co^{III}(\text{Me-salen})(\text{bzlan})_2]^+ + e \longrightarrow trans\text{-}[Co^{II}(\text{Me-salen})] + 2\ \text{bzlan}$$

The addition of an electron to the antibonding dz^2 orbital leads to the loss of the axial ligand even in weakly coordinating solvents [7, 18, 20]. The results show that the nature of the axial ligand has a strong influence on the anodic peak potentials (E_{pa}) for the first reduction process $Co^{III} + e^- \rightarrow Co^{II}$ (differing by almost 299 mV in going from MeIm to py). This is, as expected, due to the fact that the electron affinity of cobalt(III) in these complexes increases with increasing pK_b (decreasing the basicity) of the axial ligand; therefore, the corresponding reduction potentials shift to more positive values for axial ligands of lower basicity. In fact, there is a good correlation between the pK_b of the axial ligand, the position of the first d-d transition in the electronic spectra, and the first cathodic potential (E_{pc}, Co(III/II)) of the complexes. These results are in agreement with those obtained for similar Co(III) complexes reported in the literature [7, 18, 20].

The second electrochemically quasi-reversible reduction couple observed at –1.458 V (ΔE = 83 mV) is related to the following one-electron transfer process:

$$trans\text{-}[Co^{II}(\text{Me-salen})] + e \longrightarrow trans\text{-}[Co^{I}(\text{Me-salen})]^-$$

The cyclic voltammograms of **2-7** in the absence of axial ligands show features similar to those observed for complex **1** (**Table 6**).

The reversibility of the first redox process in many Co(III) Schiff base complexes is greatly influenced by many controlling factors including the concentration of the ancillary ligands [7, 18]. In an attempt to examine the reversibility of (Co^{III}/Co^{II}) reduction process, the electrochemistry of *trans*-$[Co^{III}(\text{Me-salen})(\text{bzlan})_2]PF_6$ was carried out in the presence of excess bzlan. **Fig. 4** shows the cyclic voltammogram of *trans*-$[Co^{III}(\text{Me-salen})(\text{bzlan})_2]PF_6$ (**1**)

at different bzlan concentrations. In the absence of additional bzlan the first reduction process, (Co^{III}/Co^{II}), is electrochemically irreversible (ΔE = 718 mV). Upon addition of excess bzlan ligands, the oxidation wave of Co(II) is shifted towards more negative potentials by 0.556 V (Fig. 6) (ΔE = 162 mV). Apparently, the electrode process is preceded by a reversible chemical reaction (eq. (1)), leading to the formation of the six-coordinated adduct.

$$[Co^{II}(\text{Me-salen})] + \text{excess bzlan ligand} \longrightarrow [Co^{III}(\text{Me-salen})(L)_2]^+ + e^- \quad (1)$$

The redox behavior of the Co(II/I) couple is not significantly influenced by the addition of excess axial ligand and can be regarded as approximately independent.

3.5 Antibacterial properties

The in vitro antibacterial activities of the Schiff base and the complexes were tested against two Gram-positive and two Gram-negative bacteria by disc diffusion methods using Kanamycine and Chloramphenicol as reference standards, according to the Clinical and Laboratory Standards Institute (CLSI) interpretive criteria [38]. **Table 7 and Table 8** show the MICs and the MBCs for the studied ligand, complexes and two standard compounds, against the bacterial strains, respectively.

Table 7. MIC of synthesized compounds against growth of bacteria (µg/ml).

Compound	Gram Negative Bacteria		Gram Positive Bacteria	
	E.coli	S. typhi	S. aureus	B.subtilis
Ligand	6000	6500	6200	5000
Complex 1	4000	4200	3800	3500
Complex 2	5000	5200	6000	4800
Complex 3	3000	2000	2500	1000
Complex 4	4000	2000	3500	3000
Complex 5	4000	4500	3500	3000
Complex 6	4200	4000	4200	3000
Complex 7	5000	3500	3000	3000
Kanamycine	3.8	3.2	3	3.6
Chloramphenicol	5.3	4	3.5	4

Table 8. MBC of synthesized compounds against growth of bacteria (µg/ml).

Compound	Gram Negative Bacteria		Gram Positive Bacteria	
	E.coli	S. typhi	S. aureus	B.subtilis
Ligand	8000	8000	7000	5200
Complex 1	5000	5000	4200	4000
Complex 2	6200	5500	6200	5200
Complex 3	5000	3000	3000	2000
Complex 4	5000	2500	4500	3000
Complex 5	5200	5000	4000	5000
Complex 6	5000	4000	5000	4000
Complex 7	5500	5000	4000	3500
Kanamycine	3.8	3.2	3	3.6
Chloramphenicol	5.3	4	3.5	4

A comparative study of the ligand and complexes indicates that complex 3 exhibits higher antimicrobial activities against the Gram negative and Gram positive bacteria than the free ligand, thus the axial ligands may be useful in management of such infections. The enhanced antibacterial activity of this axial ligand may be due to the presence of oxygene atom, and so, the complex of **3** exhibits antimicrobial activities against the Salmonella Typhi and Bacillus subtilis. In general, the antibacterial results show that the majority of the metal complexes were more active than their respective Schiff bases. It is evident from the MBC data that the antimicrobial activities of complex **6** against Gram negative and Gram-positive bacteria tested, are higher as compared with ligand and other complexes. This enhancement in the activity is suggested to be possibly due to an efficient diffusion of the metal complexes into the bacterial cell or interaction with the bacterial cell walls [39].

4. Conclusion

We have prepared seven Co(III) complexes of Me-salen with two ancillary ligands in the trans-positions. The main features of the coordination and redox chemistry of the *trans*-$[Co^{III}(Me\text{-}salen)(L)_2]^+$ complexes have been illustrated by the combination of spectral, structural, and electrochemical measurements. Electrochemical studies have revealed that the first reduction process Co(III/II) is irreversible and strongly influenced by the nature of the axial ligands. This process becomes quasi-reversible upon the addition of excess axial ligands.

The Co(II)/Co(I) couple is reversible and insensitive to moderate concentrations of axial ligands. The antimicrobial data exhibited that most of Co^{III} complexes are more active than those of corresponding free ligand against bacterial.

Acknowledgements

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Supplementary material unjustified

Detailed crystallographic data have been deposited in CIF format. CCDC 715071 (**1**) and 715072 (**5**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Figure captions

Fig. 1. Structural drawing of complex **1** showing 50% ellipsoids. Hydrogen atoms, PF_6 anion and $CHCl_3$ solvent molecule are omitted for clarity.

Fig. 2. Structural drawing of complex **5** showing 50% ellipsoids. Hydrogen atoms and PF_6 anion are omitted for clarity.

Fig. 3. Cyclic voltammogram corresponding to *trans*-$[Co^{III}(Me\text{-}salen)(bzlan)_2]PF_6$ in acetonitrile solution stored for 48 h. at 293 K. Scan rate: 100 mV s^{-1}. c = 4.0×10^{-3} M.

Fig. 4. Cyclic voltammograms of *trans*-$[Co^{III}(Me\text{-}salen)(bzlan)_2]^+$ at different benzylamine concentrations ratios (0, a), (10, b), (30, c), (50, d), (70, e), (80, f), (90, g), (100, h), in acetonitrile containing 0.1 M TBAH as supporting electrolyte at 298 K. Scan rate 100 mV s^{-1}, c = 4.0×10^{-3} M.

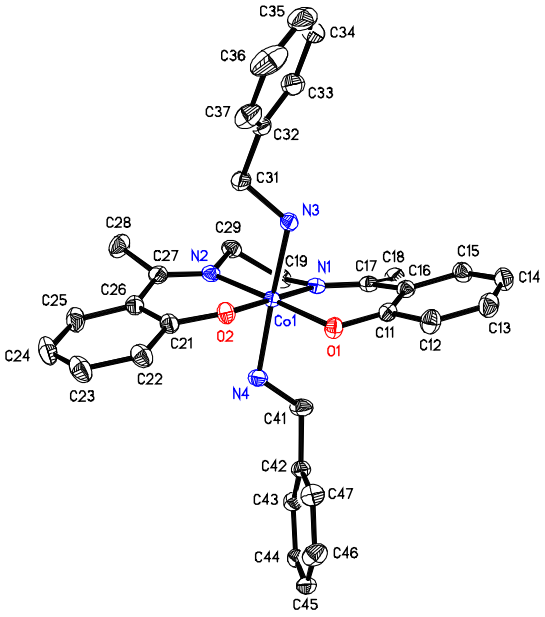

Fig 1

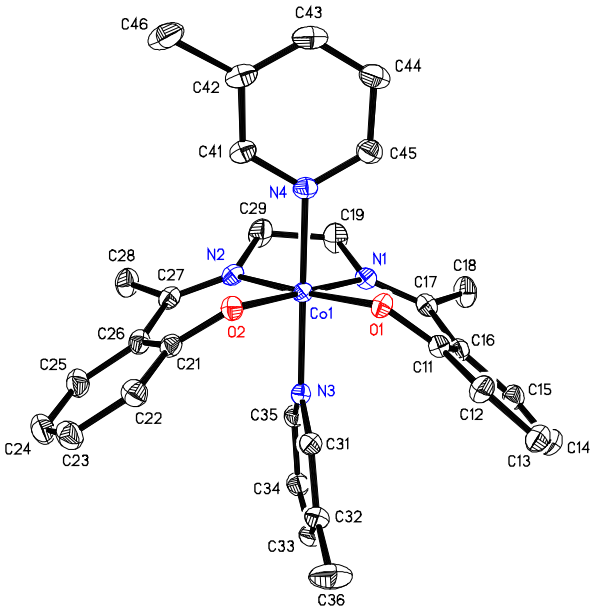

Fig 2

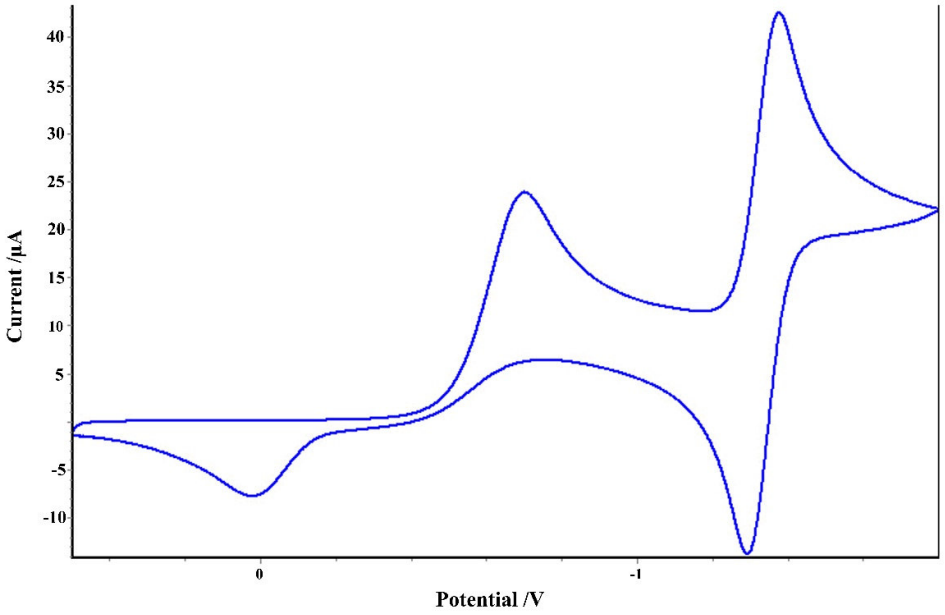
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Fig 3

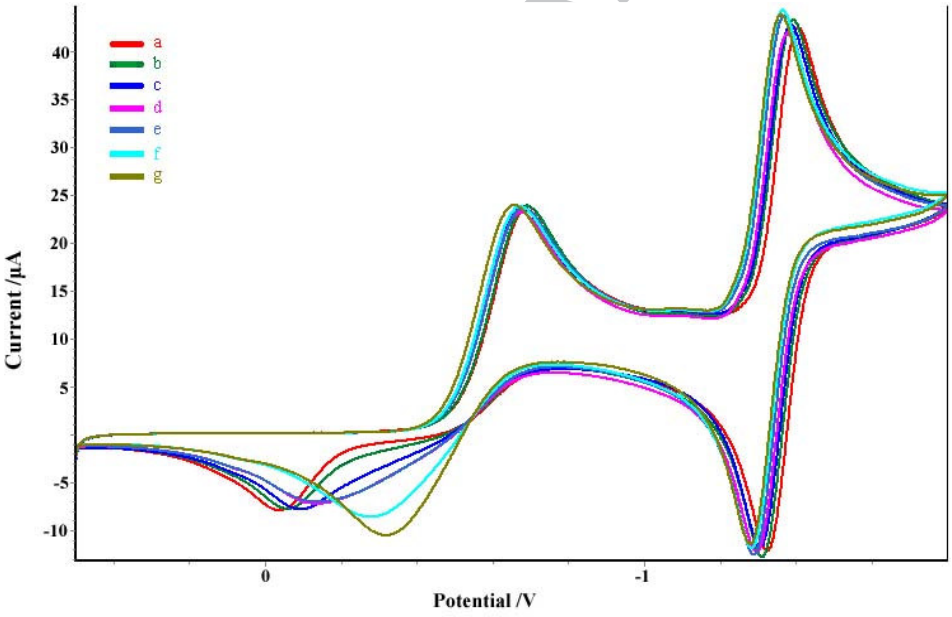
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Fig 4

Graphical abstract