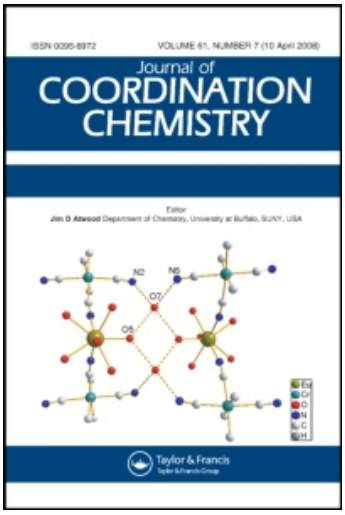

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Synthesis, characterization, antibacterial, and thermal studies of unsymmetrical Schiff-base complexes of cobalt(II)

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Synthesis, characterization, antibacterial, and thermal studies of unsymmetrical Schiff-base complexes of cobalt(II)

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Cobalt(II) complexes of a new series of unsymmetrical Schiff bases have been synthesized and characterized by their elemental analyses, melting points, magnetic susceptibility, thermogravimetric analysis, differential scanning calorimetry, infrared (IR), and electronic spectral measurements. The purity of the ligands and the metal complexes are confirmed by microanalysis, while the unsymmetrical nature of the ligands was further corroborated by ^{1}H-NMR. Comparison of the IR spectra of the Schiff bases and their metal complexes confirm that the Schiff bases are tetradentate and coordinated *via* N_2O_2 chromophore. The magnetic moments and electronic spectral data support square-planar geometry for the cobalt(II) complexes. The complexes were thermally stable to 372.3°C and their thermal decomposition was generally *via* the partial loss of the organic moiety. The Schiff bases and their complexes were screened for *in vitro* antibacterial activities against 10 human pathogenic bacteria and their minimum inhibitory concentrations were determined. Both the free ligands and cobalt(II) complexes exhibit antibacterial activities against some strains of the microorganisms, which in a number of cases were comparable with, or higher than, that of chloramphenicol.

Keywords: Cobalt(II); Unsymmetrical Schiff base; Antibacterial activities, MIC

1. Introduction

Schiff-base complexes of transition metals are of particular interest to inorganic chemists because their structural, spectral, and chemical properties are often strongly dependent on the nature of the ligand structure [1–6]. Coordination complexes with substituted salicylaldehydes have shown diverse structures and properties generating a variety of stereochemistries and a wide range of bonding interactions [7–10]. Schiff-base metal complexes are specifically of interest in bioinorganic chemistry because many of these complexes provide biological models in understanding the structure of biomolecules and biological processes [11]. Naturally occurring dioxygen carriers and storage proteins contain a transition metal ion to which dioxygen can reversibly bind, e.g., iron (haemoglobin) and copper (haemocyanin). Such systems have been modeled by a number of Schiff-base complexes [12–14]. Some cobalt(II) Schiff-base complexes are also able to bind reversible dioxygen and they have been used as simplified models in the study of reversible binding of dioxygen by its natural transporters [12–14].

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The synthesis and characterization of symmetrical tetradentate Schiff-base complexes of cobalt have been thoroughly studied and reported in the literature [1, 15–17], but only a few unsymmetrical complexes are available [18–20]. We have recently synthesized unsymmetrical Schiff bases (H_2L^1–H_2L^4) from 2-hydroxy-1-naphthaldehyde, *o*-phenylenediamine, and salicylaldehyde or substituted salicylaldehyde and characterized their oxovanadium(IV) complexes [21]. This investigation was undertaken to study the effect of the substituents on salicylaldehyde on the stereochemistry and biological activity of metal(II) complexes. In this article, we report cobalt(II) complexes (CoL^1–CoL^4) of the unsymmetrical ligands and their antimicrobial studies. Single crystal of the complexes could not be isolated from any solutions. However, analytical, spectroscopic, and magnetic data enable us to propose possible structures. The complexes investigated are reported for the first time.

2. Experimental

2.1. *Materials*

All reagents and solvents were of the analar/spectroscopic grades and used as received. Ethanol, methanol, 5-chlorosalicylaldehyde, 5-nitrosalicylaldehyde, 3-ethoxysalicylaldehyde, 2-hydroxy-1-naphthaldehyde, salicylaldehyde, *o*-phenylenediamine, and cobalt(II) acetate tetrahydrate were purchased from Aldrich Sigma company.

2.2. *Preparation of the compounds*

Procedures for the preparation of the unsymmetrical Schiff bases have been reported in [21]. The cobalt(II) complexes were prepared by the addition of 3 mmol of $Co(CH_3COO)_2 \cdot 4H_2O$ (0.53 g), dissolved in hot absolute methanol (60 mL) by stirring 3 mmol of the respective unsymmetrical Schiff base in methanol (40 mL). The color of the mixture was changed instantly. The mixture was refluxed for 3 h and the precipitated solids were filtered, washed with cold methanol, and allowed to dry in a desiccator over silica gel.

2.3. *Physical measurements*

Microanalytical data were obtained on a Perkin Elmer model 2400 Series II CHNS/O elemental analyzer for C, H, and N. Infrared (IR) spectra were recorded on a Bruker FT-IR tensor 27 spectrophotometer directly on small samples of the compounds from 200 to 4000 cm^{-1}. Electronic absorption spectra of the complexes, recorded from 200 to 1100 nm on freshly prepared $CHCl_3$ and DMSO solutions, were measured on a Cary Model 50 spectrophotometer. Thermogravimetric analysis (TGA) was carried out at 15°C min^{-1} heating rate using a Perkin Elmer Pyris 6 TGA up to 700°C in a closed perforated aluminum pan. The differential scanning calorimetry (DSC) analysis was carried out at 20°C min^{-1} up to 450°C using a Perkin Elmer DSC 4000 series, which was calibrated with indium metal. Both TGA and DSC were run under N_2. Melting points were determined on a Barnstead/Electrothermal digital melting point apparatus and are

left uncorrected. Magnetic susceptibility measurements were made on powdered samples using a Sherwood Scientific magnetic susceptibility balance. $Hg[Co(SCN)_4]$ was used as the calibrant and corrections for diamagnetism were calculated from Pascal's constants.

2.4. *Biological studies*

2.4.1. Bacterial strains. The metal complexes and ligands were individually tested against a penal of microorganisms (Gram negative and Gram positive), namely *Enterobacter cloacae* (ATCC 13047), *Serratia marcescens* (ATCC 9986), *Acinetobacter calcaoceuticus* (Aci1), *Acinetobacter calcaoceuticus anitratus* (Aci2), *Salmonella* spp., *Staphylococcus aureus* (ATCC 6538), *Bacillus pumilus* (ATCC 14884), *Bacillus subtilis*, *Staphylococcus epidermidis*, and *Micrococcus kristinae*. The organisms were obtained from the Department of Microbiology, University of Fort Hare, South Africa.

2.4.2. Disc diffusion assay. Antibacterial activity of the ligands and metal complexes were carried out using the disc diffusion method described by Bauer *et al.* [22]. Bacteria were maintained on Mueller–Hinton nutrient agar at 4°C. Molten Mueller–Hinton agar was inoculated with a broth culture of the respective bacterial strains and poured over sterile 90 mm petri dishes. Cobalt(II) acetate, metal complexes, and ligands were dissolved in DMSO to a final concentration of $10\,mg\,mL^{-1}$ and sterile Whatman No. 1 (6 mm) discs were separately impregnated with each sample to be tested at $5.0\,mg\,mL^{-1}$ and placed on the inoculated agar. The plates were incubated at 37°C for 24 h and the zones of inhibition were measured at the end of the incubation period. Chloramphenicol was used as the standard antibiotic for reference drug.

2.4.3. Minimum inhibitory concentration. The minimum inhibitory concentrations (MIC) of the ligands, metal complexes, and cobalt(II) acetate that showed antibacterial activities were determined using the 96-well micro-plate dilution method described by Eloff [23]. The serial plate concentrations were 5.0, 2.5, 1.25, 0.625, 0.313, 0.157, 0.078, and $0.039\,mg\,mL^{-1}$ for the compounds. Standard antibiotic (chloramphenicol) was used as positive control. Bacteria were grown for 18 h in nutrient broth and cultures of 108 colony forming unit (cfu) mL^{-1} were used and incubated for 24 h at 37°C. As an indicator of bacterial growth, 40 μL of $0.2\,mg\,mL^{-1}$ *p*-iodonitrotetrazolium (INT) solution was added to each well and incubated at 37°C for 30–120 min. The colorless tetrazolium salt was reduced to a red-colored product by the biological activity of the organisms, thereby making the inhibition of bacterial growth visible as a clear well. MIC values were recorded as the lowest concentration in which there was no bacterial growth. Each treatment was replicated thrice.

3. Results and discussion

3.1. *Synthesis*

The synthetic methodology followed for preparing the unsymmetrical Schiff bases was developed in our laboratory and their formation and characterization have been

published in [21]. ^{1}H NMR data revealed that the unsymmetrical Schiff bases were isolated, while microanalyses confirmed the purity of all the ligands as formulated. The formation of the symmetrical *N*,*N*′-bis(naphthalidene)-*o*-phenylenediamine or *N*,*N*′-bis(3- or 5-substituted-salicylidene)-*o*-phenylenediamine and the unsymmetrical analogue could be distinguished from the microanalytical data since they have different molecular masses.

The cobalt(II) complexes were prepared by refluxing the relevant unsymmetrical Schiff bases with $Co(CH_3COO)_2 \cdot 4H_2O$ in methanol (figure 1). All the cobalt(II) complexes formed are brown with melting points greater than 250°C. The complexes are stable in air, insoluble in water but slightly soluble in chloroform and DMSO. The purity of the Schiff bases and their metal complexes, as formulated, were established by microanalyses. The analytical data, color, percentage yields, and melting points of the compounds are presented in table 1.

3.2. *IR spectra*

The assignments of the significant IR spectral bands of the ligands and their metal complexes are presented in table 2. Due to the unsymmetrical nature of the ligands and the complexes, two bands were observed for each of the following bonds: ν(C=N), ν(C–O), ν(Co–N), and ν(Co–O), taking their origin from the different aldehydes [21]. The positions of ν(C=N) bands of the ligands appeared at 1610–1621 and 1567–1583 cm^{-1}, shifted to lower frequencies at 1603–1606 and 1571–1578 cm^{-1}, respectively, upon complexation, indicating the involvement of both nitrogens of the azomethine groups in coordination [24]. On the other hand, the ν(C–O), which occur at 1313–1333 and 1276–1289 cm^{-1} for the ligands were moved to higher frequencies by 12–30 cm^{-1} after complexation, which indicates that the shifts are due to the coordination of the phenolic oxygen of the ligand to the metal ion [5]. Thus, it can be concluded that the Schiff bases are tetradentate ligands coordinating *via* the azomethine *N* and the phenolic *O*.

Metal–ligand vibrational modes are very sensitive to substituent effects [25, 26]. This was proposed on the basis of isotopic labeling studies (^{15}N- and ^{18}O-labeling). The substituent effects were based on the position of substitution rather than the nature of the substituents. The ν(M–O) bands are observed to exhibit higher vibrational frequencies than ν(M–N) bands for the meta-substituents, while the order is reversed for *para*-substituents regardless of the nature of the substituents. It was suggested that the transmission of the substituent effects in the Schiff-base complexes are propagated largely by a mesomeric mechanism. The substituents in the complexes reported in this study are located in the 3- and 5-positions on the salicylaldehyde ring and it is expected that ν(Co–O) bands would be greater than ν(Co–N) bands, as shown in table 2. The new bands observed in the complexes in the region 453–580 and 508–554 cm^{-1} were assigned to ν(Co–N) while 463–575 and 423–428 cm^{-1} were attributed to ν(Co–O) [26].

3.3. *Electronic spectra*

The electronic spectral measurements were used for assigning the stereochemistries of metal complexes based on the positions and number of d–d transition peaks. For four-coordinate cobalt(II) complexes, either a square planar or a tetrahedral

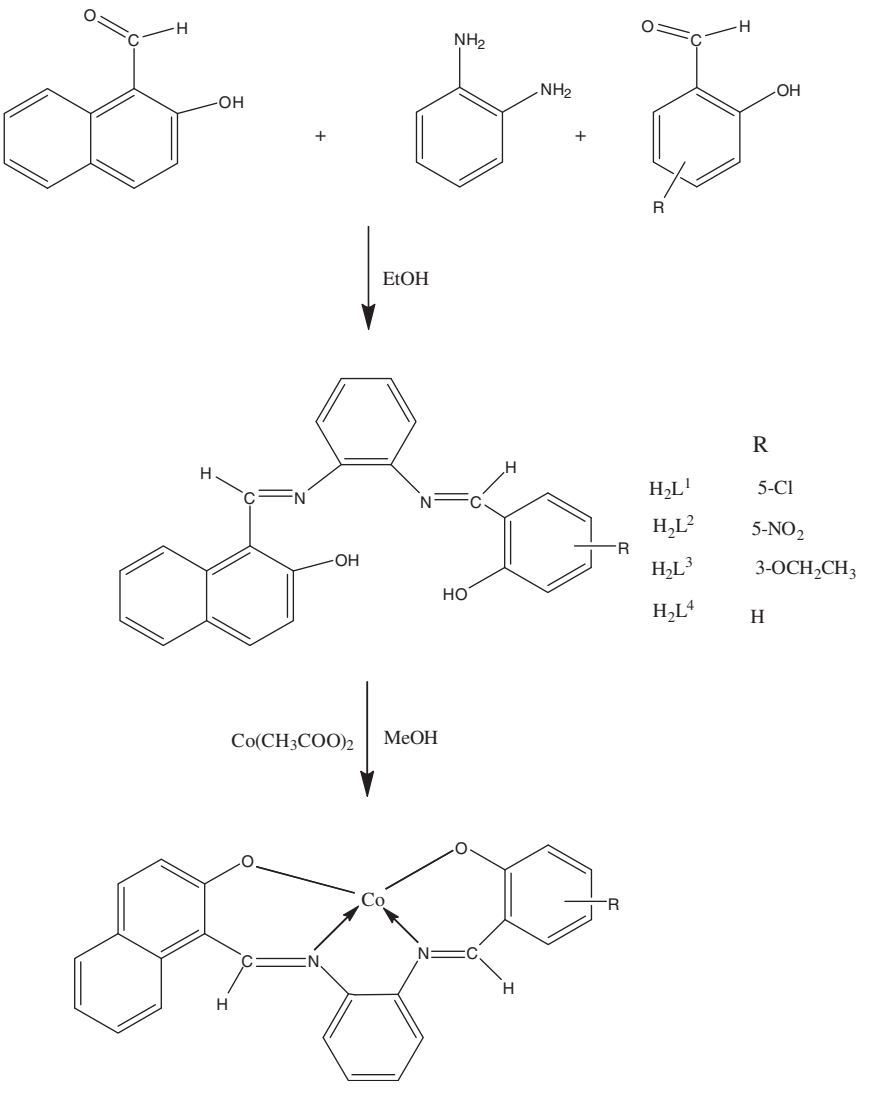

Figure 1. Preparation of the Schiff bases and their metal complexes.

configuration is possible. On the basis of electronic spectra, together with the magnetic moments, it is possible to differentiate between these two configurations. The electronic absorption spectra of complexes were recorded in 10^{-5} mol L^{-1} DMSO and chloroform in the range of 200–1100 nm at room temperature; the results are summarized in table 3 and figure 2.

Electronic spectra of all the cobalt(II) complexes in $CHCl_3$ are very similar and consist of three bands, one each at 18,587–18,939, 22,272–22,779, and 24,876–25,575 cm^{-1}, which clearly indicate the low-spin square planar/distorted square planar geometry of the complexes [27, 28]. This is also corroborated by the observed effective magnetic moment of the complexes. The other intense bands

Table 1. Physical properties, analytical data, and magnetic moment of the compounds.

Compound	Empirical formula	Formula weight	Yield (%)	Color	m.p. (°C)	Microanalysis (Calcd) %C	%H	%N	μ_{eff} (B.M.)
H_2L^1	$C_{24}H_{17}N_2O_2Cl$	400.58	91.5	Orange-yellow	194–195	71.60 (71.90)	4.73 (4.28)	6.60 (6.99)	
CoL^1	$C_{24}H_{15}N_2O_2ClCo$	457.5	93.2	Brown	>250	63.17 (62.95)	3.20 (3.30)	5.81 (6.12)	2.61
H_2L^2	$C_{24}H_{17}N_3O_4$	411.12	86.2	Orange-yellow	134–135	69.69 (70.05)	4.23 (4.17)	10.12 (10.22)	
CoL^2	$C_{24}H_{15}N_3O_4Co$	468.04	89.5	Brown	>250	61.97 (61.53)	3.10 (3.23)	8.63 (8.98)	2.59
H_2L^3	$C_{26}H_{22}N_2O_3$	410.16	71.9	Orange-yellow	135–136	76.34 (76.07)	5.51 (5.41)	6.79 (6.83)	
CoL^3	$C_{26}H_{20}N_2O_3Co$	467.08	94.7	Brown	>250	66.62 (66.80)	4.30 (4.32)	5.91 (6.00)	2.23
H_2L^4	$C_{24}H_{18}N_2O_2$	366.14	78.4	Orange-yellow	187–188	78.41 (78.66)	4.81 (4.95)	7.62 (7.65)	
CoL^4	$C_{24}H_{16}N_2O_2Co$	423.05	91.8	Brown	>250	68.31 (68.08)	3.65 (3.81)	6.16 (6.62)	2.36

Table 2. Selected IR spectral bands of the compounds.

Complex	ν(C=N)	ν(C–O)	ν(M–N)	ν(M–O)
CoL^1	1604, 1578	1326, 1288	453, 508	575, 423
H_2L^1	1611, 1583	1313, 1276	–	–
CoL^2	1603, 1574	1363, 1319	454, 539	568, 428
H_2L^2	1621, 1567	1333, 1289	–	–
CoL^3	1606, 1577	1342, 1314	475, 548	568, 428
H_2L^3	1610, 1569	1316, 1283	–	–
CoL^4	1603, 1571	1337, 1313	580, 554	463, 428
H_2L^4	1615, 1568	1313, 1286	–	–

Table 3. Electronic spectral data of the cobalt(II) complexes.

Compound	Solvent	d–d Transitions (cm^{-1}) ($\varepsilon\,cm^{-1}\,mol^{-1}$)	C.T.	Ligand[a]
CoL^1	$CHCl_3$	18,939 (77), 22,523 (205)		31,949 (228)
		24,876 (273)		40,323 (606)
	DMSO	25,126 (236)	29,586 (183)	
CoL^2	$CHCl_3$	18,587 (59), 22,272 (153)		31,447 (202)
		25,575 (227)		40,816 (364)
	DMSO	25,063 (333)		36,101 (363)
CoL^3	$CHCl_3$	18,868 (93), 22,523 (233)	28,902 (270)	40,323 (675)
		24,876 (279)	30,675 (274)	
	DMSO	25,063 (228)	29,412 (238)	
CoL^4	$CHCl_3$	18,832 (94), 22,779 (250)		31,546 (277)
		25,189 (337)		41,494 (668)
	DMSO	25,445 (263)	29,586 (215)	

[a]The spectra were noisy in the UV and some of the bands in the region could not be extracted.

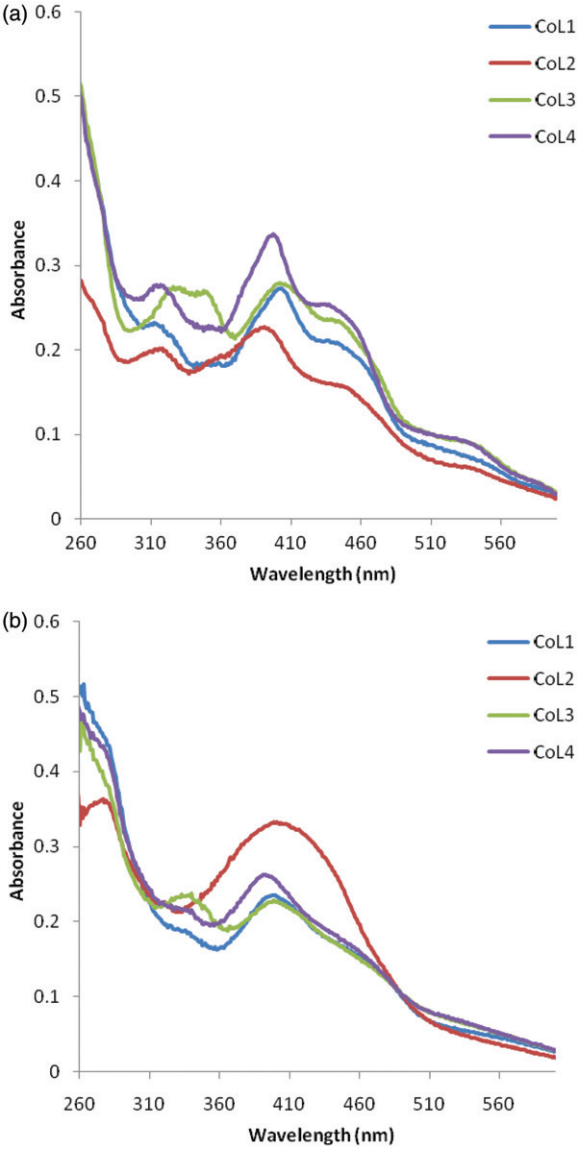

Figure 2. Electronic spectra of cobalt(II) complexes: (A) [complexes] = 10^{-5} mol L^{-1} in $CHCl_3$; (B) [complexes] = 10^{-5} mol L^{-1} in DMSO.

between 28,902 and 41,494 cm^{-1} are due to charge-transfer transitions. The electronic spectra of all the complexes in DMSO displayed a single d–d transition at 25,063–25,445 cm^{-1} and a charge-transfer transition at 29,412–36,101 cm^{-1}. The appearance of a single d–d transition in DMSO is attributed to the effect of coordination of solvent which alters the stereochemistry to form low-spin six-coordinate distorted octahedral [29]. The slight differences in the peaks observed in the spectra of these complexes in both solvents are due to the substituent effects of the different substituents on the salicylaldehyde ring.

Table 4. Thermoanalytical results (TGA, DSC) of the cobalt(II) complexes.

Compounds	T^a (°C)	Weight loss[a] (Calcd) (%)	Endothermic $t_{min}{}^b$ (°C)	ΔH^b (kJg^{-1})	Exothermic $t_{max}{}^b$ (°C)	ΔH^b (kJg^{-1})	Decomposition assignment
CoL^1	422.0	17.7 (16.6)	420.2	0.0206	422.8	−0.1282	C_6H_4
CoL^2	409.8	13.5 (13.7)	—	—	420.1	−0.3448	C_5H_4
CoL^3	372.3	27.8 (28.3)	253.2	0.0439	382.6	−0.0552	C_6H_4, HCN, C_2H_5
CoL^4	398.3	19.1 (18.0)	340.3	0.0833	399.0	−0.0406	C_6H_4

T^a: Onset decomposition temperature from TGA.
[a]Data obtained from TGA; 15°C min^{-1} under N_2 gas.
[b]Data obtained from DSC; 20°C min^{-1} under N_2 gas.

3.4. *Magnetic moment*

The observed magnetic moments for cobalt(II) complexes are generally diagnostic of the coordination geometry about the metal ion. The room temperature magnetic moments of low-spin square-planar cobalt(II) complexes are between 1.9 and 2.9 B.M., arising from one unpaired electron plus an apparently large orbital contribution. Both tetrahedral and high-spin octahedral cobalt(II) complexes possess three unpaired electrons but may be distinguished by the magnitude of the deviation of effective magnetic moment from the spin-only value. The octahedral and tetrahedral cobalt(II) complexes are reported to have magnetic moments between 4.9–5.2 and 4.2–4.8 B.M., respectively [30]. The effective magnetic moments of all the cobalt(II) complexes reported here lie in the range of 2.23–2.61 B.M. (table 1), corresponding to one unpaired electron for square-planar stereochemistry around d^7 cobalt(II) ion [27].

3.5. *Thermal analysis*

The thermal decomposition characteristics of the cobalt complexes were studied using thermal analytical techniques (TGA and DSC) under nitrogen. The thermal behaviors of the complexes are summarized in table 4. The results show good agreement with the formulas suggested from the analytical data (table 1). Their thermal behavior is typified by CoL^3 (figure 3).

In the TGA, decomposition was generally *via* partial loss of the organic moiety. The complexes were thermally stable up to 372.3°C, which indicates that the complexes have excellent stability. The TGA data showed that CoL^1 was stable up to 422.0°C. Above this temperature, the thermogram showed a weight loss of 17.7% (Calcd 16.6%), accompanied by an exothermic peak at 422.8°C on the DSC thermogram, which reasonably accounted for the loss of C_6H_4. The decomposition curve of CoL^2 proceeded with single degradation step at 409.2°C displaying a weight loss of 13.5% (Calcd 13.7%) corresponding to the removal of C_5H_4. The DSC thermogram of the complex exhibits an exothermic peak at 420.1°C corresponding to the loss of C_5H_4. The TGA thermogram of CoL^3 showed a mass loss of 27.8% (Calcd 28.3%) with a corresponding exothermic peak at 382.6°C on the DSC curve, which could be attributed to the loss of C_6H_4, HCN, and C_2H_5. The thermogram of CoL^4 showed a mass loss of 19.1% (Calcd 18.0%) at the onset decomposition temperature at 398.3°C with a corresponding exothermic peak at 399.0 on the DSC curve, which indicates the loss

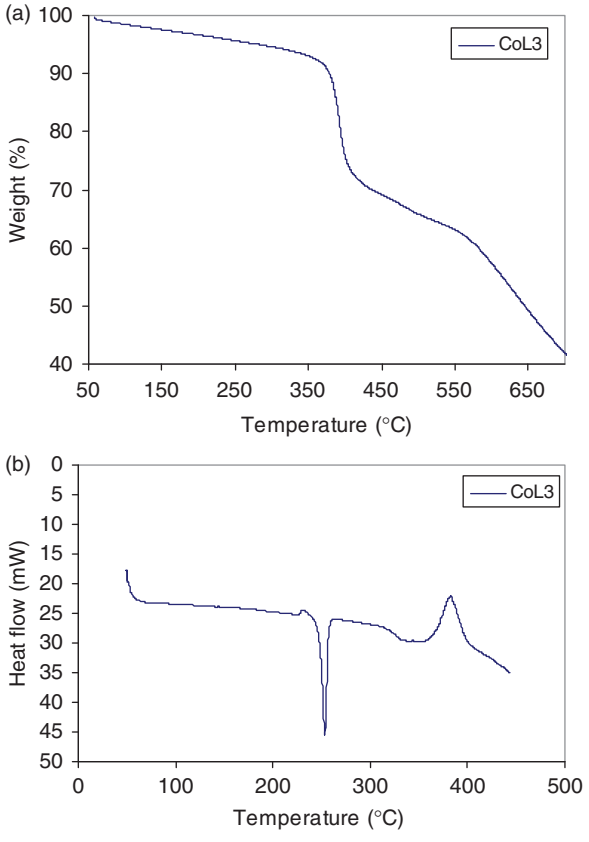

Figure 3. Thermal analysis of CoL^3: (A) TGA and (B) DSC.

of C_6H_4. The order of thermal stability of the cobalt(II) complexes, $CoL^1 > CoL^2 > CoL^4 > CoL^3$, showed that the complexes with electron-withdrawing substituents on the salicylaldehyde were more stable than the other complexes.

The thermal behaviors, including melting temperature and enthalpy of fusion, were determined by DSC. DSC data (table 4) showed a melting process (endothermic peaks) at 420.2°C, 253.2°C, and 340.3°C for CoL^1, CoL^3, and CoL^4, respectively; CoL^2 decomposed without melting. The DSC thermogram of CoL^1 showed a sharp endothermic peak and one exothermic peak in which the melting and the onset of decomposition are partially superimposed. All complexes investigated decomposed (exothermic peaks) with ΔH values ranging from as low as $-0.040.6\,kJ\,g^{-1}$ for CoL^4 to as high as $-0.344.8\,kJ\,g^{-1}$ for CoL^2 (table 4).

3.6. *Biological properties*

Antibacterial activity of the ligands and complexes were tested *in vitro* against 10 human pathogenic bacteria. The activities were compared with that of chloramphenicol,

a standard broad-spectrum antibiotic for bacterial strains. The effect of cobalt(II) acetate was also reported. The compounds were tested at a concentration of 5 mg mL^{-1} in DMSO using the paper disc diffusion method. The growth inhibition zones were measured in diameter (mm) and the results are reproduced in table 5 and figure 4. The susceptibility zones measured were clear zones around the discs killing the bacteria. All the Schiff bases and their complexes exhibit varying degrees of inhibitory effects on the growth of the tested bacterial species.

H_2L^1 and H_2L^2 were effective against all the bacteria, with inhibitory zones of 8–12 and 9–14 mm, respectively. H_2L^3 was effective against eight organisms, with inhibitory zones of 8–10 mm, whereas H_2L^4 was effective against five organisms with inhibitory zones of 9–10 mm. The cobalt(II) complexes of all the Schiff bases were highly effective against all the bacterial strains with zones of inhibition of 10–24 mm. The cobalt(II) acetate used for the synthesis of cobalt complexes was effective against six organisms, with inhibitory zones of 8–10 mm. Consequently, the enhanced activity of the metal complexes arises from coordination.

MIC values of the 10 bacteria strains used in this study are presented in table 6. Antibacterial MIC less than 1 mg mL^{-1} is considered to be an acceptable antibacterial activity [31]. When the Schiff bases and the corresponding complexes have the same MIC, the complexes are considered to be more active because of the lower molar concentration of the complexes due to higher molecular mass. Both the free ligands and cobalt(II) complexes exhibit pronounced antibacterial activities against some bacterial strains, in a number of cases comparable or even higher with that of chloramphenicol.

The Schiff bases were biologically active. However, the metal complexes, CoL^2 and CoL^3, showed enhanced antibacterial activity against more bacterial strains than their corresponding ligands. The increased activity of the metal chelates can be explained by Overtone's concept [32] and Tweedy's theory [33]. Metal complexes also disturb the respiration process of the cell and thus block the synthesis of proteins, which restricts further growth of the organism [32]. The enhanced activity of these cobalt(II) complexes are in good agreement with previously published data on cobalt complexes [34–36].

The biological activities of the complexes follow the order: $CoL^2 > CoL^3 > CoL^1 > CoL^4$. From the above results, it seems that the substitution on the salicylaldehyde ring enhances the biological activity of the complexes because the complex without a substituent has the lowest antibacterial effect. The order of activity observed in these complexes is reversely obtained for oxovanadium(IV) complexes of this same ligand system. The insulin mimetic activity of the oxovanadium(IV) complexes reported earlier showed that the substitution on the salicylaldehyde lowers the insulin-enhancing activity of the complexes [21]. The antibacterial result of the cobalt(II) acetate show activity against only *Bacillus pumilus* while six of the bacteria strains were resistant to it. In general, the antibacterial results show that the majority of the metal complexes were more active than their respective Schiff bases. However, the Schiff bases are, in a few cases, more active than the metal complexes. Cobalt(II) acetate shows low antibacterial activity in comparison with the ligands and the metal complexes. Chloramphenicol showed the lowest MIC value of < 0.0098 mg mL^{-1} against eight bacterial strains used in this study and was more active than all the compounds tested when their MIC values are compared.

Table 5. The antibacterial activities of the Schiff bases and their metal complexes.

Diameter of inhibition zone of bacteria in different compounds (mm)										
Bacterial strains	H_2L^1	CoL^1	H_2L^2	CoL^2	H_2L^3	CoL^3	H_2L^4	CoL^4	$Co(Ac)_2$	Chloramphenicol
E. cloacae	8.0 ± 1.5	20.0 ± 0.5	11.0 ± 1.5	12.0 ± 0.0	8.0 ± 1.0	16.0 ± 0.0	9.0 ± 1.5	20.0 ± 0.5	0.0 ± 0.0	20.0 ± 0.0
S. marcescens	11.0 ± 2.0	14.0 ± 1.5	14.0 ± 0.5	10.0 ± 1.0	8.0 ± 0.5	10.0 ± 1.0	0.0 ± 0.0	18.0 ± 0.5	0.0 ± 0.0	29.0 ± 1.5
A. calcaoceuticus	12.0 ± 1.0	14.0 ± 0.0	10.0 ± 2.0	14.0 ± 1.5	0.0 ± 0.0	16.0 ± 1.5	9.0 ± 2.0	20.0 ± 0.25	0.0 ± 0.0	19.0 ± 2.0
A. calcaoceuticus anitratus	12.0 ± 0.5	16.0 ± 1.0	12.0 ± 0.5	12.0 ± 1.0	8.0 ± 1.0	16.0 ± 1.0	0.0 ± 0.0	20.0 ± 0.5	0.0 ± 0.0	28.0 ± 1.0
Salmonella spp.	10.0 ± 1.0	18.0 ± 0.5	11.0 ± 1.0	16.0 ± 2.5	10.0 ± 0.5	14.0 ± 0.5	10.0 ± 1.5	20.0 ± 1.5	0.0 ± 0.0	22.0 ± 2.5
B. pumilus	9.0 ± 1.5	18.0 ± 0.0	11.0 ± 0.0	16.0 ± 0.5	9.0 ± 1.0	14.0 ± 0.25	10.0 ± 0.5	16.0 ± 0.5	10.0 ± 1.0	22.0 ± 1.0
B. subtilis	10.0 ± 0.0	14.0 ± 0.5	11.0 ± 2.0	12.0 ± 0.5	9.0 ± 0.0	16.0 ± 0.5	0.0 ± 0.0	20.0 ± 0.0	0.0 ± 0.0	23.0 ± 1.25
S. epidermidis	10.0 ± 0.5	20.0 ± 1.0	10.0 ± 0.5	16.0 ± 1.5	9.0 ± 2.5	16.0 ± 1.0	11.0 ± 1.5	24.0 ± 0.5	10.0 ± 0.5	20.0 ± 0.5
S. aureus	11.0 ± 2.5	16.0 ± 0.0	10.0 ± 1.0	14.0 ± 2.0	0.0 ± 0.0	14.0 ± 2.5	0.0 ± 0.0	18.0 ± 1.0	8.0 ± 0.5	25.0 ± 1.5
M. kristinae	8.0 ± 1.5	24.0 ± 1.0	9.0 ± 0.0	14.0 ± 1.25	9.0 ± 1.25	18.0 ± 0.0	0.0 ± 0.0	22.0 ± 0.5	10.0 ± 1.0	24.0 ± 1.25

Values are the mean ± standard deviation of the mean; Ac = acetate.

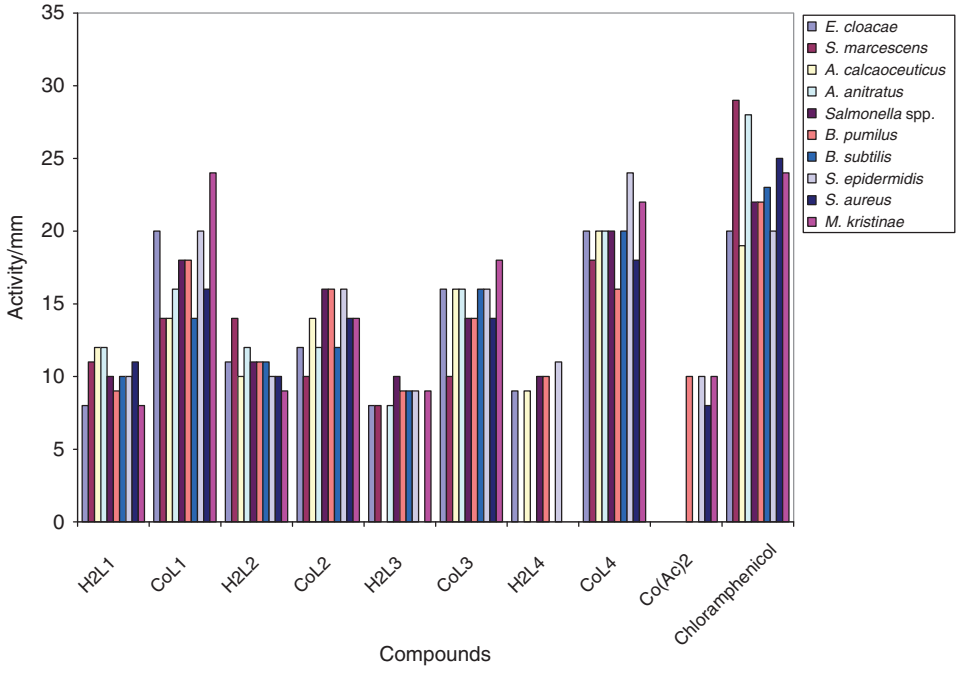

Figure 4. Histogram showing the comparative activities of the compounds.

Table 6. Antibacterial MIC of the compounds.

MIC (mmol mL^{-1})										
Bacterial strains	H_2L^1 10^{-3}	CoL^1 10^{-3}	H_2L^2 10^{-3}	CoL^2 10^{-3}	H_2L^3 10^{-3}	CoL^3 10^{-3}	H_2L^4 10^{-3}	CoL^4 10^{-3}	$Co(Ac)_2$ 10^{-3}	Chloramphenicol 10^{-3}
E. cloacae	0.40	0.35	0.39	0.09	0.76	0.34	0.11	0.09	R	3.87
S. marcescens	1.57	0.68	1.53	0.66	1.54	1.35	0.85	0.73	R	<0.03
A. calcaoceuticus	3.12	0.68	3.04	0.66	R	0.66	0.85	0.73	R	<0.03
A. calcaoceuticus anitratus	1.57	1.38	1.53	0.66	0.76	0.66	0.85	1.49	R	<0.03
Salmonella spp.	3.12	1.38	1.53	0.66	3.05	1.35	3.69	2.95	R	<0.03
B. pumilus	0.20	0.70	0.39	1.35	0.10	1.35	0.22	1.49	0.90	<0.30
B. subtilis	1.57	1.38	1.53	1.35	1.54	1.35	1.72	1.49	R	3.87
S. epidermidis	0.40	2.73	0.78	1.35	1.54	2.86	0.87	2.95	7.06	<0.03
S. aureus	1.57	1.38	1.53	1.35	0.78	0.69	1.72	0.76	14.13	<0.03
M. kristinae	1.57	1.38	3.04	1.35	3.29	1.35	3.41	2.95	7.06	0.06

R = resistant; Ac = acetate.

4. Conclusion

A series of cobalt(II) complexes involving unsymmetrical tetradentate Schiff bases derived from 2-hydroxy-1-naphthaldehyde, phenylenediamine, and salicylaldehyde or substituted salicylaldehyde have been synthesized and characterized. Comparison of the IR spectra of the Schiff bases and their metal complexes indicate that the Schiff bases are tetradentate coordinating *via* the azomethine *N* and the phenolic *O*. The electronic spectra of the complexes indicate low-spin square-planar geometry, further

corroborated by the observed effective magnetic moment of 2.23–2.61 B.M. The order of thermal stability of the cobalt(II) complexes, $CoL^1 > CoL^2 > CoL^4 > CoL^3$, shows that the complexes with electron-withdrawing substituents on the salicylaldehyde were more stable than the other complexes. The antibacterial (MIC) results showed that the majority of the Co(II) complexes were more active than the Schiff bases, arising from the coordination of cobalt(II) to the ligand.

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References

[1] S. Yamada. *Coord. Chem. Rev.*, **190–192**, 537 (1999).
[2] R. Vafazadeh, M. Kashfi. *Bull. Korean Chem. Soc.*, **28**, 1227 (2007).
[3] L.C. Nathan, J.E. Koehne, J.M. Gilmore, K.A. Hannibal, W.E. Dewhirst, T.D. Mai. *Polyhedron*, **22**, 887 (2003).
[4] I.A. Kahwa, T.C.Y. Hsieh, R.A. Laine, J. Selbin. *Inorg. Chim. Acta*, **118**, 179 (1986).
[5] M.M. Abd-Elza. *J. Chin. Chem. Soc.*, **48**, 153 (2001).
[6] N. Raman, J. Dhaveethuraja, A. Sakthivel. *J. Chem. Sci.*, **119**, 303 (2007).
[7] E. Yoshida, S. Yamada. *Bull. Chem. Soc. Jpn.*, **40**, 1395 (1967).
[8] A. Elmali, C.T. Zeyrek, Y. Elerman, T.N. Durlu. *J. Chem. Crystallogr.*, **30**, 167 (2000).
[9] A.A. Soliman, W. Linert. *Thermochim. Acta*, **338**, 67 (1999).
[10] S. Zolezzi, A. Decinti, E. Spodine. *Polyhedron*, **18**, 897 (1999).
[11] Z.H. Abd El-Wahab, M.R. El-Sarrag. *Spectrochim. Acta, Part A*, **60**, 271 (2004).
[12] T.D. Thangadurai, M. Gowri, K. Natarajan. *Synth. React. Inorg. Met.-Org. Chem.*, **32**, 329 (2002).
[13] A. Pui. *Croatica Chem. Acta*, **75**, 165 (2002).
[14] L. Casella, M. Gullotti. *Inorg. Chem.*, **25**, 1293 (1986).
[15] I.J. Sallomi, A.J. Shaheen. *Polyhedron*, **17**, 1420 (1998).
[16] M.H. Mahmoudkhani, A. Gorji, S. Dehghanpour, H.R. Bijanzadeh. *Polyhedron*, **21**, 2733 (2002).
[17] A. Ghames, T. Douadi, D. Haffar, S. Chafaa, M. Allain, M.A. Khan, G. Bouet. *Polyhedron*, **25**, 3201 (2006).
[18] S. Tan, K. Ang, L. Ng, A.G. Davies, D. Oprescu. *Transition Met. Chem.*, **15**, 459 (1990).
[19] P.J. Burke, D.R. McMillin. *J. Chem. Soc., Dalton Trans.*, 1794 (1980).
[20] G.A. Kolawole, A.A. Osowole. *J. Coord. Chem.*, **62**, 1437 (2009).
[21] A.A. Nejo, G.A. Kolawole, A.R Opoku, C. Muller, J. Wolowska. *J. Coord. Chem.*, **62**, 3411 (2009).
[22] A.W. Bauer, W.N.N. Kirby, J.C. Sherris, M. Turck. *Am. J. Clin. Pathol.*, **45**, 493 (1966).
[23] J.N. Eloff. *Planta Med.*, **64**, 711 (1998).
[24] P.E. Aranha, M.P. Do Santo, S. Romera, E.R. Dockal. *Polyhedron*, **26**, 1373 (2007).
[25] R.D. Hancock, D.A. Thornton. *J. Mol. Struct.*, **4**, 361 (1969).
[26] G.C. Percy, D.A. Thornton. *J. Inorg. Nucl. Chem.*, **34**, 3357 (1972).
[27] B.S. Manhas, B.C. Verma, S.B. Kalia. *Polyhedron*, **14**, 3549 (1995).
[28] N.V. Loginova, T.V. Koval'chuk, N.P. Osipovich, G.I. Polozov, V.L. Sorokin, A.A. Chernyavskaya, O.I. Shadyro. *Polyhedron*, **27**, 985 (2008).
[29] S. Belaid, A. Landreau, O. Benali-Baitich, M.A. Khan, G. Bouet. *Transition Met. Chem.*, **33**, 511 (2008).
[30] S. Yamada. *Coord. Chem. Rev.*, **1**, 415 (1966).
[31] N. Aligiannis, E. Kalpotzakis, S. Mitaku, I.B. Chinou. *J. Agric. Food Chem.*, **40**, 4168 (2001).
[32] N. Dharmaraj, P. Viswanathamurthi, K. Natarajan. *Transition Met. Chem.*, **26**, 105 (2001).
[33] B.G. Tweedy. *Phytopathology*, **55**, 910 (1964).
[34] M. Sönmez, M. Çelebi, A. Levent, I. Berber, Z. Sentürk. *J. Coord. Chem.*, **63**, 1986 (2010).
[35] Y.-T. Wang, G.-M. Tang, Y.-C. Zhang, W.-Z. Wan, J.-C. Yu, T.-D. Li, Y.-Z. Cui. *J. Coord. Chem.*, **63**, 1504 (2010).
[36] N. Nishat, M. Zulfequar, Asma, S. Hasnain. *J. Coord. Chem.*, **63**, 1273 (2010).