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SYNTHESIS , CHARACTERISATION AND ANTIBACTERIAL STUDIES OF ANIONIC CHELATE COMPLEXES OF MANGANESE (II) WITH VARIOUS SCHIFF'S BASE LIGANDS

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ABSTRACT

In the present study, four anionic Mn(II) complexes of various Schiff's bases such as Salicylaldehyde ethylenediamine (Sal_2en), Salicylaldehyde Orthoaminophenol (Sal OAP),Salicylaldehyde Semicarbazone (Sal Sc) and salicylaldehyde o-phenylene diamine (Sal_2phen) along with NH_4SCN ligand were synthesised. The resulting complexes were suggested to have formulae (1)$[NH_4]_2[Mn(Sal_2en)(SCN)_2]$, (2)$[NH_4]_2[Mn(SalOAP)(SCN)_2.H_2O]$, (3)$[NH_4]_2[Mn(Sal_2phen)(SCN)_2]$ and (4) $[NH_4]_2[Mn(Sal.Sc)(SCN)_2.H_2O]$.The formulae of the complexes were based on the characterisation such as its molecular weight, conductivity measurements, melting point/stability, magnetic susceptibility, UV spectroscopy and Infrared spectral studies. Interesting results were obtained revealing six coordination and chirality of the central metal ion. The antibacterial activity was studied against two Strain Gram +ve bacteria (Staphalococcus auras, Enterococcus) and two Strain Gram -ve bacteria (E.coli, P.aeruginosa) to observe their inhibiting tendency. The results showed complexes were inactive against Staphalococcus auras except for complex (3) and all the complexes have moderate or no activity against the rest microorganisms.

INTRODUCTION

Schiff bases are considered as a very important class of organic compounds, which have wide applications in various fields, such as medicine, agriculture, industries etc. Transition metal complexes with 1,10 –phenanthroline and 2, 2 –bipyridine are heavily used in petroleum refining (John *et al*, 1976). Transition metal complexes derived from a number of amino acids have been reported to have biological activity (Zahid *et al*, 2007). The quest for clear understanding of the nature of chemical bond and structure of coordination compounds has catalysed the investigative methodologies systematically. As a result of such endeavours the application of coordination chemistry has been extended to various fields such as identification and separation of chemical elements, preparation of reactor materials, extraction of rare elements and their enrichment, classification of some life processes etc. Transition metal complexes of Schiff's bases are one of the most adaptable and thoroughly studied systems. A number of scientists had been interested in investigating the biological and medicinal properties of transition metal complexes. Thomas and Parmeswaran (2002) studied the antitumour activities of Mn^{2+}, Co^{2+}, Ni^{2+} and Cu^{2+} chelates of anthracene-9-carboxaldehyde thiosemicarbazone. Murthy and Dharmaraja (2002) reported the cytotoxic activity of phenylglyoxal bis(thiosemicarbazone) against Ehrlich ascites carcinona cells . Most of the literature survey reveals that transition metal complexes generally crystallize with octahedral, tetrahedral or square planer geometry (Sleema et al, 2002). There has been extensive research on manganese (II) complexes with water ligands. The Mn-H_2O complex can be a model species for all high-spin manganese complexes, which include the majority of all Mn (II) complexes. This is because for Mn (II), the pairing energy is very high and there are only few known structures with ligands creating a sufficiently strong field to force the complex into the low-spin state. The low-spin complexes, e.g. $[Mn\ (CN)_6]^{4-}$ and $[Mn(CNR)_6]^{4-}$ (R=CH_3, C_2H_5), have been studied much less frequently than the high-spin complexes because their occurrence in biological and other systems is very rare (Bartosz Trzaskowski *et al* 2003). In the present investigation, four different Schiff's bases were synthesised by condensation of salicylaldehyde with ehtylenediamine/orthoamino phenol / semicarbazide and o-phenylene diamine. The resulting Schiff's bases were made to coordinate with Mn(II) along with N/S donor ligand such as

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SCN^-. The spectral and analytical characterization of the synthesised complexes were carried out to suggest the most plausible stereochemistry of the complexes around the Mn(II) ion. In this investigation, an antibacterial study has also been involved to follow the biological and medicinal potency of the coordination compounds synthesised.

MATERIALS AND METHODS

All chemicals used in this work were reagent grade (BDH/ Aldrich), including the metal salt $MnCl_2.4H_2O$, salicylaldehyde, ethylenediamine, Orthoaminophenol, semicarbazide, o-phenylenediamine, ammonium thiocyanate etc. The solvents like ethanol, nitrobenzene, DMSO were dried over anhydrous calcium chloride. Schiff's base (SB_1) was prepared by mixing ethylenediamine with ethanolic solution of salicylaldehyde in 1:2 molar ratio. It was then warmed, cooled and allowed to stand in a water bath for 1 hour. Then it was filtered, washed with ether and crystallised from ethanol and dried in a desiccator. Orthoamino phenol in ethanolic medium was added to ethanolic solution of salicylaldehyde in 1:1 molar ratio to prepare SB_2. The resulting solution was refluxed for half an hour, cooled and filtered when the Schiff's base separated out. It was then washed with ether and recrystallised from ethanol followed by drying in a desiccator. O-phenylenediamine was mixed with ethanolic solution of salicylaldehyde in 1:2 molar ratio to prepare SB_3. The resulting solution was refluxed for 1 hour, cooled and filtered. The resulting Schiff's base was then washed several times with ether and recrystallised from alcohol and dried in a desiccator. To prepare SB_4, Semicarbazide hydrochloride was mixed with ethanolic solution of salicylaldehyde in 1:2 molar ratio. The resulting solution was refluxed for 1 hour, cooled and filtered. The resulting Schiff's base was then washed with ether and recrystallised from alcohol and dried in a desiccator.

Metal complexes were prepared as described in the literature (Chen *et al* 1987: 1026). 0.01 mole ethanolic solution of each of the Schiff's bases synthesised was added separately to 0.01 mol (1.98 gm) aqueous solution of $MnCl_2.4H_2O$ with constant stirring and heating continuously on a magnetic stirrer followed by dropwise addition of aq.NH_3.. To the resulting solution, excess NH_4SCN solution was added dropwise. The resulting mixture was refluxed for 5 hours on a heating mantle at 65^0C. The solid complex started separating out in 2/3 days which was then filtered, washed with ethanol , ether and dried in vacuum.

Instrumentation, physico-chemical measurements and analytical estimations

The IR spectra of the ligands and their mixed ligand complexes were measured using Bruker FT-IR Spectro-Photometer in the range 400-4000 cm^{-1}. The magnetic susceptibilities of complexes were determined on Gouy balance model 7550 at 23°C. The diamagnetic corrections were made by Pascal's constant and $Hg[Co(SCN)_4]$ was used as a calibrant. UV-Visible spectra were measured in DMSO using a Japson double beam UV-Visible spectrophotometer. The molecular weight determination of the complexes was carried out by Rast's biphenyl method as described in the literature (Cowles, 1963). A HI 2314 conductivity meter was used for the conductivity measurements of the complexes in DMSO at room temperature. Melting point of the complexes was measured using a melting point apparatus.

Antibacterial activity

the antimicrobial activity of the prepared complexes were studied by the agar well diffusion method against two strain gram +ve bacteria (Staphalococcus auras, Enterococcus) and two strain gram –ve bacteria (E.oli, P.aeruginosa). The bacteria were cultured for 24 h at 37 ^0C in an incubator. Stock solutions of the compounds were prepared by dissolving (2 mg/ml) in DMSO solvent. The prepared agar medium was autoclaved at 121 ^0C for 15 min and then poured onto a pre-sterilized petridish. Petridishes containing nutrient Muller Hinton medium were seeded with 24 h culture of bacterial strains using sterile L-rod. A sterile cork borer was used to punch wells and 10 µg/ml of the prepared complexes were added from stock solution. The inoculated plates were then incubated for 24 h at 37 ^0C. After incubation, the diameter of the inhibition zone was measured and the results were recorded in millimeters (mm). The antibacterial screening concentrations of the compounds were estimated from the minimum inhibitory concentration (MIC), (Joseph *et al*. 2013).

RESULTS

The prepared complexes with four different Schiff's bases and NH_4SCN were found to be quite stable and coloured. All the synthesised complexes were insoluble in common organic solvents but were soluble in DMF and DMSO. The physical and analytical data of the complexes are presented in Table 1. The IR spectral data and uv data for the complexes are presented in Table 2.

Table 1. The physical and analytical data of the complexes

Sl. No of complexes	Complex (colour)	Mol.wt Found/calcd	M.pt (^0C)	μ_{eff} in BM Found/calcd	Molar conductance (Λ_m) mho cm^2 mol^{-1}
1	$[NH_4]_2[Mn(Sal_2en)(SCN)_2]$ (Grey)	469.12 (473.53)	235	5.72 (5.9)	185
2	$[NH_4]_2[Mn(SalOAP)(SCN)_2.H_2O]$ (black)	432.01 (436.46)	242	5.85 (5.9)	157
3	$[NH_4]_2$ $[Mn(Sal_2phen)(SCN)_2]$ (Dark Brown)	518.22 (523.59)	216	5.60 (5.9)	201
4	$[NH_4]_2[Mn(Sal.Sc)(SCN)_2.H_2O]$ (Yellow)	382.48 (388.40)	240	5.85 (5.9)	192

Table 2. The IR and UV spectral data for the complexes

Sl No	Complex	$\nu_{C=N}$	Phenolic OH	M-O	M-N	M-NCS	ν_{NH4+}	δ_{NCS} + CS (bend)	H_2O	Electronic Spectra
1	$[NH_4]_2[Mn(Sal_2en)(SCN)_2]$	1615	1539	594	462	2040	3020,3100(bp) 1435,1380 (sp)	1145.1045	----	20,000; 22700 28,300
2	$[NH_4]_2$ [Mn (SalOAP)$(SCN)_2.H_2O$]	1634	1530	581	450	2064	3138,3043 (bp) 1401 (sp)	1145,1030	3400 (bp) 837,754 (R,W)	17,857; 22,790 28,674
3	$[NH_4]_2$ [Mn (Sal_2 Phen) $(SCN)_2$]	1595	1530	564	460	2040	3149,3000(bp) 1430,1372 (sp)	1146,1025	---------	18,050; 23,750 29136
4	$[NH_4]_2$ [Mn (Sal. Sc) $(SCN)_2.H_2O$]	1644	1510	600	437	2089	3169,3013(bp) 1438 (sp)	1143,1036	3434 900.756 (R,W)	16,835; 22,800 29,100

Table 3. Antimicrobial activity of complexes in (mm) in 10 ppm DMSO solvent

complexes	S.aureus	Enterococcus	E.coli	P.aeruginosa
$[NH_4]_2[Mn(Sal_2en)(SCN)_2]$	-----------	4.8	5.1	4.6
$[NH_4]_2[Mn(SalOAP)(SCN)_2.H_2O]$	-----------	3.7	4.3	3.2
$[NH_4]_2$ $[Mn(Sal_2phen)(SCN)_2]$	5.2	8.2	7.6	9.1
$[NH_4]_2[Mn(Sal.Sc(SCN)_2.H_2O]$	-----------	6.2	5.4	6.6

Antimicrobial activity studies of the complexes are summarised in Table 3.

DISCUSSION

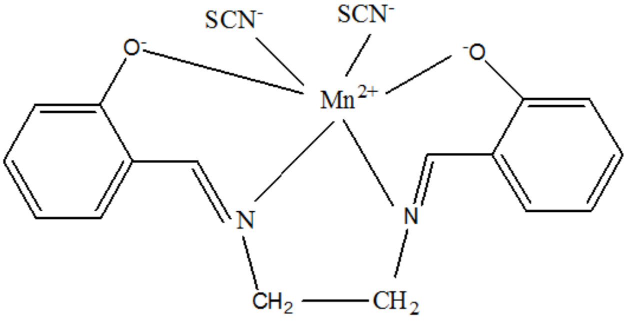
Magnetic susceptibility: Magnetic susceptibility measurements are generally diagnostic of the geometry of the coordination complexes about the metal ion. The values also support the electronic spectral measurements to suggest a plausible geometry and structure of the studied complexes. The room temperature magnetic moments of the complexes prepared during this investigation are listed in Table 1. The magnetic susceptibilities, all of which are independent of field strength, were corrected for the diamagnetic contribution of the ligands, the anions and the metal ions using Pascal's constants. The effective magnetic moment of the synthesised complex of manganese(II) is of the high-spin, d^5 state exhibiting magnetic moment in the range of 5.60- 5.85 B.M which is well within the range for a octahedral high spin complex. (Natrajan *et al* 2002, Shoemaker *et al* 1989). In an octahedral environment the ground term of Mn(II) is orbital singlet. Although there is no first-order orbital contribution to the susceptibility for this ion, there is second-order contribution due to the coupling between this state and some excited states arising from the same free ion states through the spin-orbit coupling. **(**Bayri Ali *et al* 2007).

Conductivity measurement: All the complexes show a high conductivity value which ranges in between 185-201 mho cm^2 mol^{-1} indicating the complexes to be 2: 1 electrolytic in nature (Table 1). All the complexes were found to have high melting point above 200^0C (Table 1). The molecular weight values indicate the monomeric nature of all the complexes.

Infra-red spectra: The IR spectral data for the complexes are presented in Table 2. To study the co-ordinating donor sites of the Schiff's bases to the metal ion, IR spectrum of the complexes were compared with the spectra of ligands.

Complex-1

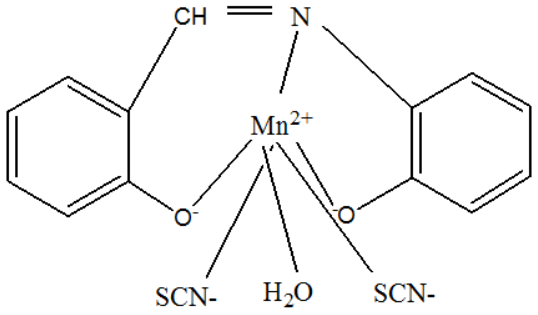
The Sciff's base, Bis-Salicylaldehyde ethylene Diamine (Sal_2en) shows bands at $3025cm^{-1}$,$1625cm^{-1}$,$1575cm^{-1}$,$1235cm^{-1}$,$1060cm^{-1}$ due to $\nu_{(C-H)aromatic}$, $\nu_{C=N}$, $\nu_{(O-H)phenolic}$, ring vibrations and ν_{C-O} and ν_{C-N} respectively (Nakamoto, 1997). On complexation, the band at $3025cm^{-1}$ remains unaltered showing the presence of $\nu_{(C-H)\ aromatic}$ in the complexes. A sharp band at $1594cm^{-1}$ - $1615cm^{-1}$ in the complex indicates the shift due to azomethine $\nu_{C=N}$. The decrease in frequency indicates a decrease in C=N bond order due to the coordination of the azomethine nitrogen to manganese. The band at $1539cm^{-1}$ confirms the coordination of phenolic oxygen to the metal atom. The ν_{C-N} stretching frequency for ethylene diamine is increased to $1085cm^{-1}$ on complexation indicating the synthesis of Sciff's base and involvement of ethylenediamine as having the donor sites (Stuart, 2004) . The coordination through oxygen and nitrogen is further supported by the bands at $594cm^{-1}$ for ν_{Mn-O} and bands at $462cm^{-1}$ for ν_{Mn-N} respectively. (Aurel Pui *et al* 2007). Therefore, the IR spectral studies suggests that the SB_1, Bis-Salicylaldehyde ethylene Diamine (Sal_2en) coordinate as a dibasic tetradentate ligand.



Complex-1

Complex-2

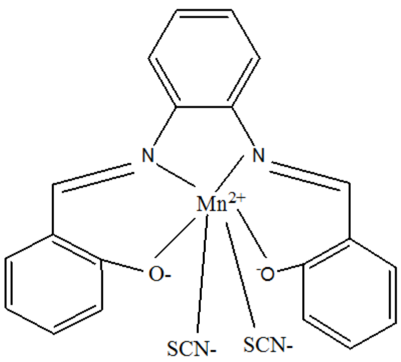
Salicylaldehyde Ortho Amino Phenol (Sal OAP) shows its characteristic spectra in the mid infra red region. A broad band at 3135-2000 cm^{-1} corresponds to the hydroxyl protons of the Schiff's base ligand which signifies the existence of a strong hydrogen bonding between the O-H and N-H groups (Syamal *et al* 1979),(Dudek *et al* 1961). However, this band disappeared in the spectra of complexes containing Sal OAP due to deprotonation and involvement of the oxygen atoms in the coordination sphere. The phenolic O-H stretching vibration bands at 1272 cm^{-1} is shifted to $1292cm^{-1}$ in the complexes, confirming the complexation via the phenolic oxygen atoms (Abdullahi Owolabi Sobola *et al* 2013). Further, in the complexes, ν(C-O) band is appearing at 1490cm^{-1} indicating the coordination of phenolic oxygen atom to the metal ion**.** (Besseler G.C and R.M Silverstein). A strong band at 1589cm^{-1} is due to azomethine ν(C=N) linkage; in the free ligand. In the complexes, the band is red shifted to 1634cm^{-1}, indicating the coordination through imine nitrogen. The coordination of the SB$_2$ was further supported by the bands at 581cm^{-1} and 450cm^{-1} which is due to ν_{Mn-O} and ν_{Mn-N} respectively (Reddy *et al* 2008).Therefore, the IR spectral studies suggests that the SB$_2$, Sal OAP coordinate as a dibasic tridentate ligand.



Complex-2

Complex-3

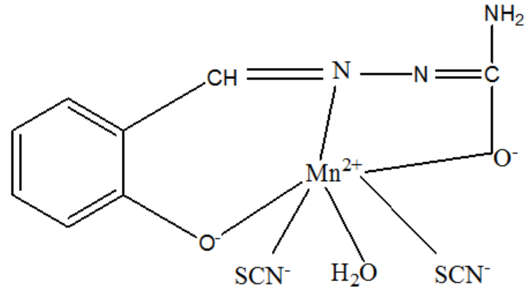
Bis salicylaldehyde O-phenylenediamine (Sal$_2$phen). A sharp band at 3150cm^{-1} corresponds to the hydroxyl protons of the ligand which indicates a strong intramolecular H-bonding between two OH groups. However the band disappeared in the complex indicating the deprotonation and involvement of the oxygen atoms in bond formation with Mn atom. The phenolic stretching vibration at 1559cm^{-1} in the ligand is reduced to 1530cm^{-1} in the complex. A strong band at 1608cm^{-1} due to azomethine ν(C=N) linkage; in the free ligands reduced to 1595 cm^{-1} in the complex, indicating the coordination through two imine nitrogen . The reduction of frequency may be attributed to conjugation in the molecule involving aromatic system. The coordination of the SB$_3$ was further supported by the bands at 564cm^{-1} and 460cm^{-1} which is due to ν_{Mn-O} and ν_{Mn-N} respectively (Reddy *et al* 2008). Therefore, the IR spectral studies suggests that the SB$_3$, Sal$_2$ phen coordinate as a dibasic tetradentate ligand.



Complex-3

Complex-4

The Sciff's base Salicylaldehyde semicarbazone(Sal Sc) shows it's characteristic spectra in the regions, 3274cm^{-1}, 3141cm^{-1},, 1583cm^{-1},1682cm^{-1}, 1487cm^{-1} assignable to ν_{NH2}, ν_{NH}, $\nu_{(C=N-N=C)}$, $\nu_{C=N}$, $\nu_{phenolic\ OH}$ vibrations respectively. On complexation, the strong bands still appearing around 3274cm^{-1} and 3149 cm^{-1} confirms the non bonding of one of the NH$_2$ groups to metal atom. There is appearance of a band at 1350cm^{-1} confirms enolisation in the ligand and a band at 1323cm^{-1} in the complex confirms the bonding through the oxygen of deprotonated enolic OH. (Nakamoto, 1997). A band at 1510cm^{-1} confirms the bonding of phenolic oxygen with the Mn atom in the complex. Furthermore, a strong band at 600cm^{-1} and 437cm^{-1} indicates the ν_{Mn-O} and ν_{Mn-N} respectively in the complex. Strong bands are appearing at 1644cm^{-1} and 1572cm^{-1} in the complex showing the presence of $\nu_{(C=N)+(O-C=N)}$ and $\nu_{C=N-N=C}$ structure in the complexes (Kasuga *et al* 2001). Therefore the IR spectral analysis indicates the coordination of the Schiff's base,SB$_4$, Sal Sc to the metal atom is through one N and two enolic O atoms and hence dibasic tridentate in nature.



Complex-4

NH$_4$SCN

For SCN$^-$, it was observed that in general class "b" metals form S-bonded complexes and class "a" metals form N-bonded complexes in their common oxidation states (Mitche *et al* 1960). Some exceptions are found where a certain metal atom can both be N-coordinated and S- coordinated in one complex forming an end to end bridge between metal atoms of same kind (Alam *et al* 2011). In the present investigation , the IR spectra of NH$_4$SCN appeared at a very strong band at 2048cm^{-1} in the free ligand, which are caused by ν_{CN} and the band at 741 cm^{-1} which was assigned as ν_{CS} (Socrates. 1980), (Kazuo N. 1997) **.** On complexation, two of the complexes, 2 and 4 (table2) were found to have bands shifted to higher frequencies i.e 2064cm^{-1} and 2089cm^{-1} and two of the other complexes 1 and 3 have bands shifted to lower frequencies at 2040 cm^{-1} indicating the involvement of nitrogen in coordination. A group of bands appearing between 1025-1146 cm^{-1} due to δ_{NCS} + CS (bend) vibrations indicates that the metal is bonded through N atom of isothiocyanato. Furthermore, a band at 3000-3169cm^{-1} and at 1372-1435cm^{-1} in the ligand was found to be unaltered in the complexes indicating the presence of NH$_4^+$ in the complex but not coordinated to the metal atom.

In addition to all the above mentioned bands, complex 2 and complex 4 was found to have strong peaks at 3400cm^{-1}-3434cm^{-1} and at 837-900cm^{-1}(rocking) and 754-756 cm^{-1} (wagging) indicating the presence of coordinated H$_2$O in the complexes.

UV spectral analysis: The electronic absorption spectral measurements were used for assigning the stereochemistry of metal ions in the complex based on the positions and number of d-d transition peaks. The UV spectra was recorded in DMSO solution. The UV spectral data is presented in Table 2. Manganese (II) is normally found in an octahedral coordination environment (Naskar *et al.,* 2005). The electronic spectra of the synthesized complexes were very much similar to each other and showed spin allowed transitions at 16835-20,000 cm^{-1}, 22,700-23,750 cm^{-1} and at 28,300-29,836 cm^{-1} regions assignable to the transitions $6A_{1g} \rightarrow 4T_{1g}$, $6A_{1g} \rightarrow 4E_g$ and charge transfer band respectively. (A.S.El-Tabi *et al.,* 2011). The nature and positions of the bands support hexa-coordinated geometry for the Mn complexes and hence concluded to be octahedral by nature. However, the exact geometry can be established from X-ray crystallographic studies of the compound.

Antibacterial study: The Schiff base containing manganese complexes were evaluated for antimicrobial activity in concentration of 10 ppm in DMSO solvent against two strain gram +ve bacteria (Staphalococcus auras, Enterococcus) and two strain gram –ve bacteria (E.oli, P.aeruginosa). The observations showed that the complexes are inactive against staphalococcus auras except for $[NH_4]_2$ $[Mn(Sal_2phen)(SCN)_2]$ with low activity against the other microorganisms. The complex $[NH_4]_2$ $[Mn(Sal_2phen)(SCN)_2]$ is comparatively more active than all the other complexes towards the microorganisms. The difference in the antibacterial activity of manganese (II) complexes studied in this work probably is associated to ligand type and its space distribution around the complex core (Sengupta *et al* 1998). The variation in the activity of different metal complexes against different microorganisms depends on the impermeability of the cell or differences in the ribosomes in the microbial cells. (Dharmaraj *et al* 2001).

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