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Nickel(II) Complexes of Schiff Bases Derived from Substituted 1,2,4-Triazole

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Complexes of nickel(II) with Schiff bases (LH_2), derived from condensing salicylaldehyde with 4-amino-3-methyl-5-mercapto-1,2,4-triazole and 4-amino-3-ethyl-5-mercapto-1,2,4-triazole, were synthesised and characterised by elemental analyses, magnetic susceptibility, UV and IR spectral data. The complexes of monoanionic as well as dianionic form of ligand molecules have been isolated in solid state by adjusting pH of the reaction medium. The electrical conductance data reveal non-electrolyte nature of the complexes. The magnetic susceptibility coupled with electronic spectral data suggest octahedral geometry for bis-ligated complexes while monoligated pyridine complexes are square-planar.

INTRODUCTION

In view of pharmacologial importance[1–3] of metal complexes of Schiff bases derived from substituted 1,2,4-triazole, we report here the preparation and characterisation of nickel(II) complexes with 4-salicylaldimino-3-methyl-5-mercapto-1,2,4-triazole (H_2-SMMT) and 4-salicylaldimino-3-ethyl-5-mercapto-1,2,4-triazole (H_2-SMMT).

EXPERIMENTAL

All the chemicals, solvents and reagents were either of E. Merck extra pure or BDH AnalaR grade. The analytical results of carbon and hydrogen were obtained from Lucknow. Nitrogen was estimated by semi-micro Duma's method. Metal content was analysed using standard method[4]. The UV spectra of complexes were recorded in dioxane and IR spectra in CsI disc at CDRI, Lucknow, Magnetic susceptibility measurements were carried out on a Gouy balance.

Preparation of Ligands

(1) *4-Salicylaldimino-3-methyl-5-mercapto-1,2,4-triazole* (*H_2-SMMT*): 4-amino-3-methyl-5-mercapto-1,2,4-triazole (AMMT) was prepared by the method given by Pujari *et al.*[5] The Schiff base was prepared by heating a mixture of AMMT and salicylaldehyde under reflux for 2 h, in equimolar ratio using ethanol as the solvent. The desired compound separated as very fine needle-like

crystals. The product was filtered and recrystallised from ethanol (m.pt. 139°C, yield 60%).

(2) *4-Salicylaldimino-3-ethyl-5-mercapto-1,2,4-triazole (H_2-SEMT):* 4-Amino-3-ethyl-5-mercapto-1,2,4-triazole (AEMT) was prepared by the method given by Pujari *et al.*[5] The Schiff base was prepared by refluxing the mixture containing equimolar quantities of AEMT and salicylaldehyde in ethanol for about 1 h. The volume of reaction mixture was reduced and allowed to stand for 4–6 h. Very fine light yellow crystals were obtained. The compound was filtered and recrystallised from ethanol (m.pt. 151°C, yield 65%).

Preparation of Complexes

The bisligated complexes were prepared by treating aqueous ethanolic solution of hydrated nickel(II) acetate with ethanolic solution of ligands in 1 : 2 molar ratio. The resulting solution was refluxed for 20 min and allowed to stand at room temperature. The yellowish green coloured complex separated out slowly on diluting it with excess of water. The monoligated pyridine complexes were prepared by treating ligands dissolved in pyridine-methanol mixture (30–40 mL methanol; 2.0 mL pyridine) with methanolic solution of hydrated nickel(II) acetate in 1 : 1 molar ratio with constant stirring. The resulting solution was refluxed on a steam bath for a few minutes and diluted with excess of water when desired complexes separated out slowly.

RESULTS AND DISCUSSION

From analytical data (Table-1) it appears that nickel(II) forms both mono- and bis-ligated complexes with ligands 4-salicylaldimino-3-methyl-5-mercapto-1,2,4-triazole (H_2-SMMT) and 4-salicylaldimino-3-ethyl-5-mercapto-1,2,4-triazole (H_2-SEMT). The bisligated products were obtained in the pH range 4–5 whereas monoligated products were obtained as pyridine adduct at pH 7–8. At lower pH these ligands are acting as monoanionic complexing molecules while at pH higher than 7 they coordinate as dianionic molecule.

In general the complexes are quite stable at room temperature. In slightly acidic medium both the ligands form complexes of the composition $[Ni(HL)_2]$ (H_2L = H_2-SMMT or H_2-SEMT) and in pyridine medium the ligands have been found to form complexes of the composition [NiLPy]. The complexes are insoluble in water and in other common organic solvents. However, the complexes dissolve appreciably in dimethylformamide (DMF). The pyridine complexes are quite stable and they do not lose pyridine molecules even at 110–120°C indicating that they are coordinated pyridines. The electrical conductance values of complexes in DMF solution were found to be almost negligible, supporting their non-electrolyte nature. The magnetic moment values of $[Ni(H\text{-}SMMT)_2]$ and $[Ni(H\text{-}SEMT)_2]$ have been found to be 3.05 B.M. and 2.95 B.M. respectively at room temperature. These μ_{eff} values indicate that Ni(II) ions are octahedrally surrounded by ligands in these complexes[6,7]. The monoligated pyridine complexes [Ni(SMMT)Py] and [Ni(SEMT)Py] are diamagnetic, hence possess square- planar geometry. The bisligated complexes display absorption bands in the regions 8500–7000, 14600–12100 and 25500–23500 cm^{-1} which may be assigned to the transitions $^3A_{2g} \rightarrow {}^3T_{2g}(\nu_1)$, $^3A_{2g} \rightarrow {}^3T_{1g}(F)(\nu_2)$ and $^3A_{2g} \rightarrow {}^3T_{1g}(P)(\nu_3)$ respectively[8]. The electronic spectral data coupled with the magnetic moment data favour octahedral geometry for these complexes. The planar complexes display a distinct band around 24000–23500 cm^{-1}. The observed band is assigned to $^1A_{1g} \rightarrow {}^1B_{1g}$ transition in planar field. The electronic absorption bands in the region 29000–28000 cm^{-1} located in the solution spectra of complexes is attributed to charge transfer transition.

TABLE-1
ANALYTICAL DATA OF Ni(II) COMPLEXES

Complex (Colour)	% Analysis, Found (Calcd.) C	H	N	S	M	μ_{eff} (B.M.)	λ_M (ohm^{-1} $mole^{-1}$ cm^2)
$[Ni(H\text{-}SMMT)_2]$ (yellowish green)	45.69 (45.74)	3.52 (3.45)	21.30 (21.33)	12.18 (12.21)	11.20 (11.18)	3.05	14
[Ni(SMMT)Py] (green)	48.61 (48.69)	3.61 (3.54)	18.94 (18.92)	8.59 (8.66)	15.84 (15.86)	diamagnetic	11
$[Ni(H\text{-}SEMT)_2]$ (yellowish green)	47.72 (47.76)	4.12 (4.00)	20.28 (20.25)	11.62 (11.59)	10.65 (10.61)	2.95	16
[Ni(SEMT)Py] (green)	49.96 (50.03)	4.01 (3.93)	18.19 (18.23)	8.41 (8.35)	15.32 (15.29)	diamagnetic	10

IR Spectra

The IR spectra of solid ligands as CsI disc do not display IR bands in the region 2700–2450 cm^{-1} expected for ν(S—H) stretch and therefore it appears that both the ligands exclusively exist in thione form[9]. The phenolic ν(—OH) group of H_2SMMT appears as broad band near 3150–3060 cm^{-1} indicating appreciable hydrogen bonding. A medium band located at 3280 cm^{-1} is assigned to ν(NH) and bands at 2960 and 2760 cm^{-1} are attributed to ν(C—H) of methyl and aldimine (C—H). The aldimino ν(C═N) of the ligand was observed at 1620 cm^{-1}. The bands located at 1605 and 1592 cm^{-1} are attributed to phenyl ring ν(C═C) and triazole ring ν(C═N) vibrations respectively.

The ν(C═N) of triazole ring and aldimino group coupled together in metal complexes and observed at 1600 ± 5 cm^{-1} indicating that aldimine nitrogen is involved in bonding in all the complexes. The thioamide bands[10] of ligand were observed at 1505, 1380, 1260 and 915 cm^{-1}. The thioamide band I and II are raised to higher frequencies while thioamide band IV shifted to lower frequency and observed at 830 ± 5 cm^{-1}. The disappearance of ν(NH) of ligand in the complexes and shift of thioamide band IV to lower frequency suggest the bonding of thioamide group by deprotonation in complexes.

The ligand displays a number of bands located at 1485, 1460, 1345, 1260, 1170, 1150, 1100, 1030, 990, 975, 805, 765 and 730 cm^{-1} attributed from different modes of IR vibration of phenyl and triazole ring as well as methyl and aldimino groups. The strong band at 1100 cm^{-1} is attributed to phenolic ν(C—O) vibration which is observed at higher frequency in complexes. In far infrared region we observed four or five prominent bands which are slightly different from the parent ligand. Thus it is very difficult to identify metal ligand vibrations in the complexes. The pyridine adduct complexes also display IR bands in the same region as the free and coordinated ligands. However, the bands observed at about 660 cm^{-1} and 445 cm^{-1} assigned to in- and out-of-plane deformation vibrations of pyridine ring are an indication of coordination[11] of pyridine to the metal ions. The other ligand (H_2-SEMT) is structurally similar to (H_2-SMMT) and, therefore, it is expected that both the ligands should have donor sites similar.

Thus, the infrared spectral studies indicated that both the ligands are bonded as tridentate chelating molecules forming bond through sulphur, phenolic oxygen and aldimino nitrogen atoms. In the case of bisligated complexes these ligands are monoanionic and sulphur is bonded in thione tautomer while in monoligated complexes these ligands are dianionic and sulphur is attached to metal atoms by deprotonation in thiol tautomer.

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