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NOTE

Transition Metal Complexes of Mn(II), Co(II) and Zn(II) with Tridentate Schiff Base and Neutral Monodentate Ligand

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Complexes of Mn(II), Co(II) and Zn(II) with tridentate Schiff base L = 2-hydroxy-1-naphthaldehyde semicarbazone (HNSC) and neutral ligand L′ = pyridine, isoquinoline, quinoline and γ-picoline with stoichiometry MLL′ (where M = Mn(II), Co(II), Zn(II), L and L′ = ligands) have been prepared and characterised by elemental analyses, molar conductance, molecular weight measurement, room temperature, magnetic susceptibility and infrared and electronic spectral measurements.

The coordination chemistry of Schiff bases having a semicarbazone unit has a special interest due to their antibacterial[1], antitumour[2] and antitubercular[3] properties. Moreover, the mixed ligand complexes with transition metal have also a number of applications. Thus in continuation with our earlier work, we report herein isolation and characterisation of some complexes using the title ligands with transition metals Mn(II), Co(II) and Zn(II).

All chemicals used were AnalaR grade. The Schiff base ligand (HNSC) was prepared by condensation of 2-hydroxy napthaldehyde and semicarbazide in 50% ethanol. The pale yellow product formed was separated and recrystallised in ethanol and dried in vacuum.

Preparation of metal complexes

An aqueous ethanolic solutions of metal chlorides (0.005 in 40 mL), Schiff base ligand (HNSC) (0.005 m in 50 mL) and (0.005 in 50 mL) neutral ligand (pyridine, isoquinoline, quinoline and γ-picoline) were mixed and refluxed on a steam bath for 1/2 h when a solid mass separated out; the products were filtered, washed with ethanol and dried in vacuum desiccator over anhydrous $CaCl_2$.

The elemental analyses were done by standard method[4]. The molar conductance in 10^{-3} M DMF solution was determined by a Systronics-303 conductivity bridge. IR spectra were recorded in nujol on a Unicam SP-200 spectrophotometer and electronic spectra were recorded using a Unicam SP-500 spectrophotometer. C, H, N were analysed by using CE-440 elemental analyzer. The magnetic susceptibility was measured at room temperature by Gouy's method using diamagnetic correction with Pascal's constant. The colour, magnetic moment and analytical data of complexes are summarised in Table-1.

The elemental analyses of the complexes suggest the stoichiometry MLL′ where M = Mn(II), CO(II) and Zn(II), L = schiff base ligand (HNSC) and L′ = neutral ligand. Molar conductance values of the complexes were found to be

15–20 ohm^{-1} cm^{2} mol^{-1} suggesting the non-electrolytic nature of the complexes. The molecular weight (Rast's camphor method) suggested the monomeric nature of the complexes. The m.p. of the complexes are above 180°C.

TABLE-1
ANALYTICAL DATA OF THE METAL COMPLEXES

Complex/Compounds	m.w.	Colour	% Analysis, found (calcd.) M	C	H	N
$C_{12}H_{11}N_3O_2$	229.00	Pale yellow	—	62.88 (62.93)	4.80 (4.95)	18.34 (18.50)
[Mn(HNSC)Py]	362.04	Light yellow	15.17 (15.50)	56.34 (56.39)	4.14 (4.50)	15.46 (15.82)
[Mn(HNSC)(IQn)]	412.10	Dark yellow	13.33 (13.50)	61.13 (61.42)	4.12 (4.52)	13.58 (13.72)
[Mn(HNSC)(Qn)]	412.10	Yellow	13.33 (13.50)	61.13 (61.42)	4.12 (4.52)	13.58 (13.72)
[Mn(HNSC)(γ-pic)]	376.07	Brick red	14.60 (14.80)	57.43 (57.50)	4.52 (4.60)	14.89 (14.92)
[Co(HNSC)Py]	366.03	Black	16.09 (16.15)	55.73 (55.80)	4.09 (4.51)	15.30 (15.50)
[Co(HNSC)(IQn)]	416.09	Deep green	14.16 (14.29)	60.55 (60.60)	4.08 (4.15)	13.45 (13.57)
[Co(HNSC)(Qn)]	416.09	Greenish blue	14.16 (14.29)	60.55 (60.60)	4.08 (4.15)	13.45 (13.57)
[Co(HNSC)(γ-pic)]	380.06	Blue	15.50 (15.59)	56.83 (56.90)	4.47 (4.60)	14.73 (14.82)
[Zn(HNSC)Py]	372.47	White	17.55 (17.70)	54.75 (54.92)	4.02 (4.19)	15.03 (15.09)
[Zn(HNSC)(IQn)]	422.53	Dirty white	15.47 (15.58)	59.62 (59.79)	4.02 (4.19)	13.25 (13.51)
[Zn(HNSC)(Qn)]	422.53	Dirty white	15.47 (15.58)	59.62 (59.79)	4.02 (4.19)	13.25 (13.51)
[Zn(HNSC)(γ-pic)]	386.50	Yellowish white	16.91 (17.00)	55.87 (55.90)	4.39 (4.50)	14.48 (14.91)

The IR spectra of ligand shows a broad and strong band at 3200–2800 cm^{-1} which represents a series of overlapping stretching vibrations corresponding to ν(NH) and ν(OH) groups. The CH stretching vibration of aromatic ring (3100–3000 cm^{-1}) seems to have been enveloped by the NH and OH stretching vibrations. It dissappears in the spectra of the metal complexes indicating the deprotonation of the ligands. The next important band due to ν(C=O) is observed at 1670 cm^{-1} of the Schiff base. The band is shifted to lower frequency region by 50–60 in all the complexes which indicates the coordination through oxygen atom of the carbonyl group. The ν(C=N) band of the Schiff base appearing at 1600 cm^{-1} is shifted and appears at 1630–1620 cm^{-1} in the complexes indicating the coordination through azomethine nitrogen[5]. The ν(OH) in plane bending vibrations of the free ligand expected around 1400 cm^{-1} is absent in the complexes indicating deprotonation of —OH group. The coordination of the Schiff base through oxygen and nitrogen atoms of the metal ion is further indicated by the appearance of ν(M—O) and ν(M—N) bands at 445–440 cm^{-1} and 520–510 cm^{-1} respectively[6]. In the IR spectra of the complexes, the band at 1580 cm^{-1} due to neutral ligand (pyridine, quinoline, isoquinoline and γ-picoline) suggests the coordination through N-atom[7]. Further, the coordination of neutral ligand through N-atom is ascertained by the appearance of band at 1540–1530 cm^{-1} due to ν(C=C)+ ν(C—N). So the IR spectral data suggest the Schiff base ligand is a tridentate ligand and coordinated through .[8, 9]

The Mn(II) complexes show the magnetic moment values of 5.78–5.95 BM which indicate the presence of five unpaired electrons as expected for a high spin divalent Mn. The electronic spectra of the complexes of Mn(II) show bands at 20471–228333, 23255–25316 and 26315–27777 cm^{-1} which can be assigned to the transition $^6A_{1g} \rightarrow {}^4T_{2g}(G)$, $^6A_{1g} \rightarrow {}^4A_{1g}{}^4E_g$ and $^6A_{1g} \rightarrow {}^4T_{2g}(D)$ respectively[9]. The spectral data and magnetic moment value suggest the tetrahedral structure of the complexes[10].

The Co(II) complexes possess magnetic moment values 3.99–4.03 BM. The electronic spectra show two bands at 9000 cm^{-1} and 15000 cm^{-1} which can be assigned to $^4A_{2g} \rightarrow {}^4T_{1g}(K)$ and $^4A_{2g} \rightarrow {}^4T_{1g}(P)$ transitions respectively. The spectral data and magnetic moment values suggest tetrahedral geometry for the Co(II) complexes. As expected Zn(II) complexes are diamagnetic. The elemental analysis and IR spectra suggest the tetrahedral structure for the Zn-complexes.

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