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SYNTHESIS AND STRUCTURAL CHARACTERIZATION OF OXOVANADIUM (IV), Mn (II), Fe (II), Fe (III), Cr (III), Co (I), Ni (0) and Hg (II) COMPLEXES WITH N-ETHOXYCARBONYL 4-CHLOROBENZENE THIOCARBOXAMIDE

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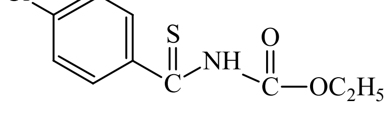
ABSTRACT

In this paper, we have reported the synthesis of some complexes of N-Ethoxycarbonyl 4-Chlorobenzene Thiocarboxamide (MNH) with VO (IV), Mn (II), Fe (II), Fe (III), Cr (III), Co(I), Ni(O) and Hg (II). These complexes have been characterized by analytical magnetic. Thermogravimetric and spectral (IR, UV and visible) studies and their structures are proposed.

Key words: Oxovanadium, N-Ethoxycarbonyl 4-chlorobenzene thiocarboxamide.

INTRODUCTION

Although, transition metal complexes of N-Ethoxycarbonyl pyrrole-2 thio carboxamide are well known[1-3]. Comparatively, much less work has been done on the metal complexes of N-ethoxycarbonyl 4-chlorobenzene thiocarboxamide (MNH) (I). No previous work on transition metal complexes of MNH is reported. Thus, we report here the preparation and characterisation of VO (IV), Cr (III), Mn (II), Fe (II), Fe (III) Co (I), Ni(0), and Hg (II), complexes of MNH.



(MNH)

This ligand can function as either neutral or anion with nitrogen, sulphur and oxygen

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*Author for correspondence; E-mail: amit2010mishra@gmail.com as potential donor atom. Both have four centered with O, N, S atoms as potential donor atoms obviously, their simultaneous participation in complex formation is virtually impossible. This may thus form monomeric or polymermic complexes. There are various ways in which MNH can coordinate with transition metal ions. In case the bonding with metal ions takes through oxygen or sulphur, their behaviour might be parallel to these of β-diketons and related ligands.

EXPERIMENTAL

All chemicals used were BDH or equivalent reagents. N-Ethoxycarbonyl, 4-chlorobenzene thiocarboxamide here after reffered as MNH was prepared as described in the literature[4] and dichlorobis triiphenyl phosphine iron (II), hydridotetrakis (triphenylphosphite) cobalt (I) and tetrakis (triphenyl phosphite) nickel (0) were prepared according to methods described in the literature[5-7].

Synthesis of the complexes

The complexes M(MN)Clx(H_2O)y [M = Mn (II), Cr(III), Fe(III), x = 1 or 2; y = 2 or 3] and $VO(MN)_2$ have been prepared by refluxing the ligand (1 mmol) in ethanol (25 mL) for ~ 3 hrs, and then adding an ethanol (25 mL) solution of the metal chloride (1 mmol). The mixture was then refluxed on a water bath for ~ 3 hrs, which resulted in the formation of a precipitate. The complex $[Hg(MNH)_2Cl_2]$ was isolated by mixing an ethanol (20 mL) solution of $HgCl_2$ (1 mmol) and ligand (2 mmol, 20 mL). A light yellow precipitate immediate formed. All the complexes prepared above were separated by centrifuging repeatedly, washing with ethanol and finally with ether, and drying in vacuo over P_2O_5.

The dichloro (MNH) bis (triphenylphosphine) iron (II) complex, $[Fe(MNH)Cl_2(PPh_3)_2]$, was isolated when dichlorobis (triphenylphosphine) iron (II) (1.25 g ~ 1 mmol) was dissolved in benzene (30 mL) by warming and to this a benzene solution of MNH (0.2 g 1 mmol in 10 mL) was added. The reaction mixture was refluxed for ~3 hrs and the resulting redish brown solution concentrated to half of its original volume. On addition of petroleum ether (15 mL, 40-60°), a green precipitate formed.

To prepare hydrido (MNH) triphenylphosphite) cobalt (I), $[CoH(MNH)P(OPh)_3]$, to a solution of $[CoH(P(OPh)_3)_4]$ (0.5 g in 20 mL CH_2Cl_2), MNH (0.3 g ~ 1.5 mmol in 15 mL ethanol) was added with costant stirring. After stirring for ~ 2 hrs and concentrating at low pressure to ~ 15 mL, petroleum ether (20 mL, 60-80°) was added to produce shining brown crystals. Mono(MNH)bis(triphenylphosphite) nickel(0), $[Ni(MNH)(P(OPh)_3)_2]$ was prepared using a similar method, where $[Ni(P(OPh)_3)_4]$ was used in a place of $[CoH(P(OPh)_3)_4]$ to give brown crystals.

All the complexes prepared above were centrifuged, washed with petroleum ether (40-60° or 60-80°) and dried in vacuo.

Analyses of the complexes

Metal, sulphur chloride and phosphorus were analyzed by literature procedures[8,9]. The analytical data are given in Table 1.

Table 1: Analytical data, colour, melting point, magnetic moment and % yield of MNH complexes

Complexes	Colour	m.p. (°C)	Analytical Found (calcd.) %							Magnetic moment μ_{eff}
			Metal	C	H	N	S	Cl	P	
$[VO(MN)_2]$	Light green	160^d	9.30 (9.27)	2.10 (2.18)	0.15 (0.18)	2.30 (2.55)	5.75 (5.82)	6.40 (6.46)		1.70
$[Cr(MN)(H_2O)_2Cl_2]$	Green	180^d	13.30 (13.00)	2.85 (3.00)	0.19 (0.25)	3.38 (3.50)	7.90 (8.00)	8.70 (8.87)		3.50
$[Mn(MN)(H_2O)_3Cl]$	Dirty green	210^d	14.50 (14.24)	3.05 (3.11)	0.20 (0.25)	3.54 (3.63)	8.21 (8.30)	9.17 (9.21)		5.65
$[Fe(MNH)Cl_2(PPh_3)_2]$	Green	155	11.30 (11.26)	2.40 (2.42)	0.17 (0.20)	2.79 (2.82)	6.40 (6.45)	7.10 (7.16)	5.89 (6.00)	5.18
$[Fe(MN)(H_2O)_2Cl_2]$	Green	190^d	14.01 (13.82)	2.90 (2.97)	0.22 (0.24)	3.40 (3.46)	7.89 (7.92)	8.76 (8.79)		5.70
$[CoH(MNH)P(OPh)_3]$	Brown	185	12.50 (12.43)	2.50 (2.53)	0.46 (0.21)	2.90 (2.95)	6.71 (6.75)	7.40 (7.49)	6.28 (6.33)	Dia
$[Ni(MNH)(P(OPh)_3)_2]$	Brown	180	9.15 (9.11)	1.82 (1.86)	0.14 (0.15)	2.12 (2.17)	4.89 (4.97)	5.48 (5.51)	4.60 (4.66)	Dia
$[Hg(MNH)_2Cl_2]$	Light yellow	> 270	26.50 (26.42)	1.52 (1.58)	0.11 (0.13)	1.80 (1.84)	4.19 (4.22)	4.59 (4.68)		Dia

d = decomposed

Physical measurement

The magnetic susceptibilities of the complexes were determined at room temperature at room temperature on a Gouy balance using $Hg[Co(NCS)_4]$ as the calibrant and experimental magnetic susceptibilities were corrected for diamagnetism[10]. Electronic spectra of the ligand and complexes were recorded on a Cary – 17 D in chloroform. Infrared spectra of the ligand and the complexes in KBr were obtained on a Perkin-Elmer spectrophotometer

Model 580. Melting points of the complexes reported are uncorrected and were observed on a Fisher-Johns melting point apparatus.

RESULTS AND DISCUSSION

All the complexes were found to be non-ionic and soluble in CH_2Cl_2, $CHCl_3$, DMF and DMSO. Assuming that the metal ions adopt normally preferred geometeries in their complexes, the analytical data (Table 1) suggests the bidentate nature of MNH in all the complexes except Hg (II) where it acts as monodentate neutral ligand. Irrespective of whether the ligand is bidentate or monodentate, it can coordinate with metal ions through any two or one of the five donor atoms viz., nitrogen, oxygen and sulphur.

The spectral studies of the ligand and its complexes were carried out to explore possible modes of linkages in the complexes.

Magnetic susceptibility measurements

The complexes of Cr (III) and Fe (III) were found to be paramagnetic and exhibited magnetic moments of 3.50 and 5.65 B.M., respectively, which are typical of high spin species. The presence of ligand (bidentate), two water molecules and two chloride ions in the inner coordination sphere makes these complexes hexa-coordinate. It is therefore, assumed that these metal ions form hexa-coordinated, octahedral, high spin complexes. The complexes of Fe (II) and Mn (II) exhibited the magnetic moments 5.18 and 5.7 B.M., respectively. The magnetic moment of the Fe (II) complex is slightly lower than the observed value (generally high spin Fe (II) complexes exhibited a magenetic moment value larger than 5.2 B.M.). It is possibly due to either distortion from octahedral geometry or solid state effecs. Further, the value of magnetic moment of Mn (II) complexes is the same in both the octahedral and tetrahedral environments of the ligand, sinse the 6_S ground state persisits in both the symmetries[11]. The number of ligands around these metal ions is five (one bidentate) and six coordinated octahedral geometry is assumed for these metal ions.

The magnetic moment of the VO(IV) complexes is 1.70 B.M., corresponding to one unpaired electron. The electronic spectrum of the complex is characteristic of square pyramidal geometry[12].

The complexes of Hg (II), Ni(0) (d^{10}) and Co (I) (d^8) were found to be diamagnetic. Since the number of ligands is four (all monodentate in the Hg (II) complex), and three (one bidentet in the Ni (0) and Co (I) complexes), it is assumed that these metal ions are four - coordinated tetrahedral (Hg (II) and Ni (0)) and square planner (Co (I)).

Electronic spectral studies

UV spectrum of the ligand in $CHCl_3$ exhibited bands at 22210, 27310, 39310 and 42670 cm^{-1}. The bands at 22210 and 27310 cm^{-1} have been assigned to $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions[2]. The bands at 39310 and 42670 cm^{-1} whose position did not shift on complextion were characteristics of the substituted benzene ring and consistant with IR spectral data. In the spectra of the complexes having PPh_3 and $P(OPh)_3$, the characteristics bands due to $\pi \rightarrow \pi^*$ transitions of the phenyl group have also been oserved.

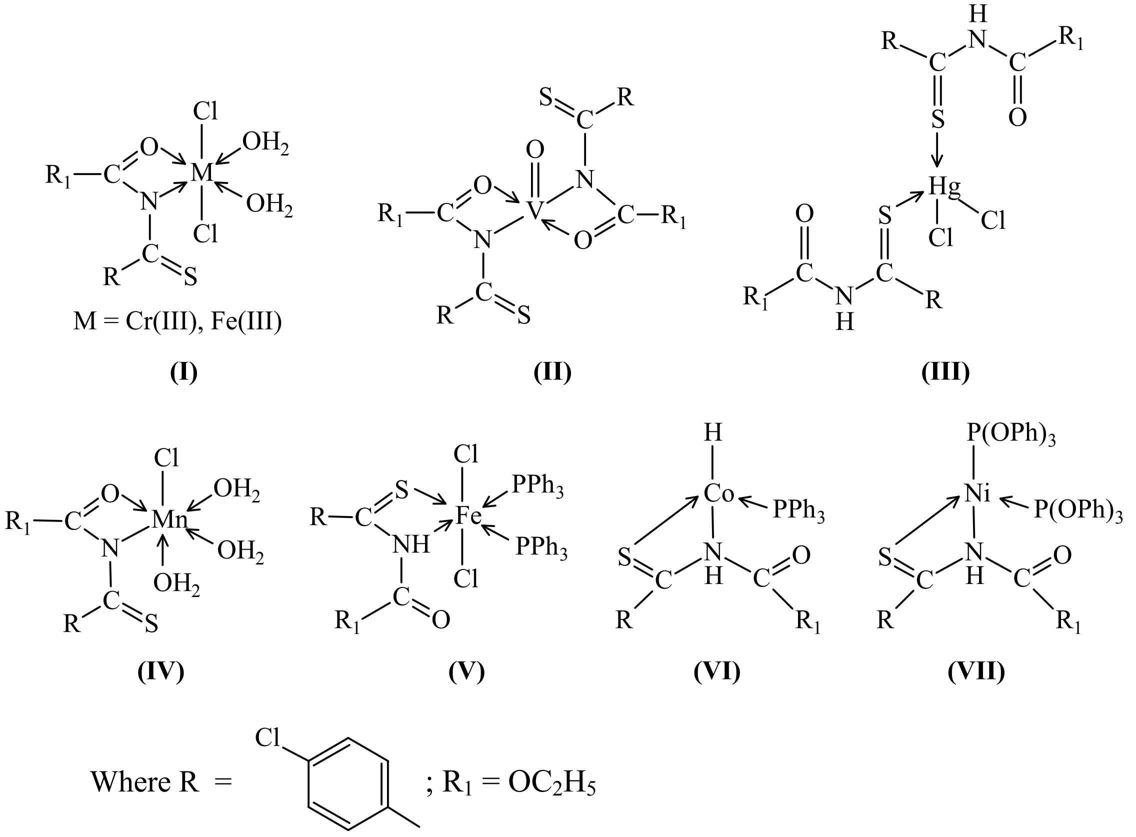

Fig. 1

The UV and visible spectrum of the Cr(III) complex shows bands at 16510, 19410, 24210 and 37310 cm^{-1}. The very high intensity of bands at 24200 and 27300 cm^{-1} indicates that these are M→L charge transfer and intraligand bands, respectively. However, the weak bands at 16510 and 19410 cm^{-1} are assigned to ${}^4A_{2g}(F) \rightarrow {}^4T_{2g}$ (F) and ${}^4A_{2g}(F) \rightarrow {}^4T_{1g}(F)$, respectively, The third characteristic band due to ${}^4A_{2g}(F) \rightarrow {}^4T_{1g}(P)$ is not observed, possibly due to the presence of a very intense charge transfer band around 28000 cm^{-1}. These are characteristics bands of Cr (III) complexes[13].

The absorption bands at 16110 ($^6A_{1g} \rightarrow {}^4T_{2g}(G)$, 24410 (M→L) and 27350 cm^{-1} (intraligand band) in the spectram of Fe (III) complex are inconsistent with its octahedral geometry[14,15].

The spectra of Ni (0) and Hg (II) complexes did not exhibit any band in visible region. In the case of Co (I), the intense charge transfer band in the visible region obscures all the weak d-d transitions bands. The spectrum of these complexes shows one band at 27510-27910 cm^{-1} (in the case of Hg (II) and Ni (0)) and two band at 22410 and 27310 (for Co (I)). These have been assigned as either due to charge transfer or intraligand bands. The spectrum of the VO(IV) complex showed four bands at 14110, 15650, 24410 and 27340 cm^{-1}. The bands at 14110 and 15650 cm^{-1} are assigned[16,17] to dxy → dyz, dxz, typical of square pyramidal geometry of a VO(IV) complex.

Thermogravimetric analysis of the complexes of Cr(III), Fe(III)

Thermogravimetric analysis of these complexes reveal interesting features and corroborate some assumptions made on the basis of infrared spectral studies. In the Cr (III) and Fe (III) complexes the mass loss starts at 135°C and there is a sharp inflexion between 160-170°C with a mass los of 10.4 to 10.5% indicating the presence of two coordinated water molecules (theoretical mass loss for two water molecules is 10.0-10.1%). The thermogroms of the Mn (II) complex show two inflexions and expulsion of three water molecules in two steps. Removal of the first molecule of water is slow and that of the second and third is rapid. The mass loss starts at 125°C and a sharp inflexion is observed at 140°C with a mas loss of 5.75% corresponding to the elimination of one water molecule (theoretical mass loss for one water molecule is 5.27%). The second inflextion is observed at 170°C with a mass loss of 16.5% (the theoretical mass loss is 15.8%). Further, the bands appearing in the region of 1050-1125 cm^{-1} in the IR spectra of these comlexes due to rocking modes of coordinated water disappear from the spectra of the complexes when heated upto 180^{o}C. This provides strong evidence for coordinated water molecule.

Infrared spectral studies

The IR spectra of the complexes were quite complicated because of the extensive mixing of various modes of vibrations in the ligand. The systematic shift of the bands, which can be assigned with some certainity, has been used to deduce the bonding of MNH involved in complex formation. These bands are grouped under the following headings for the sake of convenience in discussions.

IR spectra of M(MN) $Cl_x(H_2O)$ y {M = Mn (II), Cr (III), Fe (III): x = 1 or 2; y = 2 or 3} and VO $(MN)_2$ complexes. The shift in the band position in the IR spectra of these complexes have been found to be similar. The characteristics IR bands of the 4-chlorobenzene moiety were present in the spectrum of the ligand[18] and did not shift in the spectra of the complexes (maximum shift ± 5 cm^{-1}). This indicates that the chloro group of the Benzene moiety is not participating in the bond formation. Further, it is highly unlikely for the oxygen atom of the (O – Et) group to participate in the complex formation. Assuming the bonding in complexes with the –C(S) NHC(O)-moiety of the ligand, major shifts in the positions of thioamide and amide bands are expected. The following are the general observations in their spectra.

(i) The ν (NH) of the ligand at 3370 cm^{-1} disappeared in the spectra of all the complexes suggesting the deprotonation of the ligand.

(ii) The amide band I ν CO 1770 cm^{-1} is shifted to lower wave numbers ($\Delta \nu = 40$ cm^{-1}) indicating the involvement of carbonyl oxygen in bond formation[19].

(iii) The positions of the thioamide bands I and II having contributions from ν (CN), δ (NH) and those of amide bands II and III in the region 1500-1100 cm^{-1} either did not shift[20] or the shifts were too small to draw any definite conclusion from their direction .

(iv) Thioamide band IV at 875 cm^{-1}, due to ν (C=S) of the ligand ,shifted slightly towards higher wave numbers, suggesting noninvolvement of thiocarbonyl sulphur in the bond formation.

(v) A weak band at 845 cm^{-1} due to ν (NH) of the cis form of the -NHCO group[21] disappeared in the spectra of the complexes.

(vi) Three new bands observed in the regions 290-325, 290-310 and 270-320 cm^{-1} in the spectra of the complexes, which are absent in spectrum of the ligand are tentatively assigned to ν (M-N)[22,23] ν (M-O)[22,23] and ν (M-Cl)[24] modes, respectively.

(vii) A strong band at 970 cm^{-1} in the spectrum of the VO(IV) complex is tentatively assigned to the ν (V=O) mode[25].

(viii) A medium intensity band appearing in the region 1050-1125 cm^{-1} in the spectra of Cr (III), Fe (III) and Mn (II) complexes has been assigned to the rocking modes of coordinated water.[26]

Hg (II) complexes

(i) Thioamide band (IV) due to ligand at 875 cm^{-1} shows negative shift (-30 cm^{-1}).

(ii) The positions of the bands due to ν (NH) and ν (NH) 3370, 3145, 630 and 600 cm^{-1}), the amide I band at 1775 cm^{-1} and ν (C – OEt) band at 1190 cm^{-1} did not shift, indicating no linkage of the metal with the NH and CO groups .

(iii) The bands having contributions from ν (CN) (thioamide band I and II, amide band II and III), shifted towards higher wave numbers by 15 cm^{-1}

(iv) A new band appeared around 320 cm^{-1}, which is assigned to ν (M-S)[27].

Fe (II), Co (I) and Ni (0) complexes

(i) The lignad band at 3370 cm^{-1} due to ν (NH) shifted towards lower wave numbers and appeared around 3310 cm^{-1} suggesting increased electronegativity of the nitrogen atom of the -C(S)NH C(O) -moiety and absence of deprotonation in the complexes.

(ii) The thioamide band I and II (arising due to coupled vibrations of δ (NH) and ν (CN) at 1500 and 1310 cm^{-1} shifted towards higher wave number, 1520 cm^{-1} and 1325 cm^{-1}, respectively.

(iii) The broad bands at 1050 and 870 cm^{-1} of the free ligand shifted towards lower wave number (~20 cm^{-1}) in the spectra of the complexes. These bands have been assigned to the thioamide band III having major contibutions from ν (C-C), ν (C-N) and ν (C=S) in the normal coordinate. The shift in the positions of these bands towards lower wave numbers in the complexes further confirmed the bonding of the metal ion through thiocarbonyl sulphur.

(iv) In the spectra of the complexes, the positions of the ligand band at 495 cm^{-1} assigned to δ (C=S), shifted towards lower wave numbers (~20 cm^{-1}).

(v) The characteristics bands of triphenylphosphine were found in the spectra of the complexes.

(vi) The non-ligand bands occurring in the regions 325 and 300 cm^{-1} in spectra of complexes are tentativety assigned to ν (M-N) and ν (M-S) modes, respectively[28,29]. Thus, on the basis of analytical, spectral (IR, UV) and magnetic measurement data, the following tentavie structures have been assigned to the complexes (I – VII in Fig. 1).

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