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## SYNTHESIS, CHARACTERIZATION AND ANTIBACTERIAL ACTIVITY OF SOME TRANSITION METAL COMPLEXES WITH THIOUREA DERIVATIVES

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Transition metal complexes of Mn(II), Co(II) and Ni(II) ions with 2-hydroxyphenylthiourea, 2-carboxyphenylthiourea and 4-methyl-phenylthiourea have been synthesized and characterized on the basis of elemental analyses, conductivity and magnetic measurements and from their IR spectral studies. The complexes have the general formula:  $K_2[M_2(L^{2-})_2(NO_3)_2]$ ,  $L^{2-}$  = Dinegative deprotonated form of the ligand, 2-hydroxyphenylthiourea;  $[M(L)_2NO_3]$ , where  $L$  = 4-methylphenylthiourea and  $[M_2(L^-)_2(NO_3)_2]$ , where  $L^-$  = Uni-negative deprotonated form of the ligand, 2-carboxyphenylthiourea, with 2-hydroxyphenylthiourea and 2-carboxyphenylthiourea, Mn(II), Co(II) and Ni(II) metal ions form 5-coordinate bridging complexes whereas 4-methylphenylthiourea gives rise to 4-coordinated complexes with the same metal ions. The antibacterial activity of the ligands and their complexes have been tested with *Bacillus subtilis*. Some complexes show higher activity than that of the free ligand value whereas in some cases the activity decreases. Some complexes were found to retain the same activity as that of the ligand.

**Key words:** Metal complexes, Thiourea ligands, Antibacterial activity.

### Introduction

Metal complexes with multidentate nitrogen-sulphur donor ligands have been widely investigated [1-4] as such complexes have been found to be potential fungicidal [5], antiviral [6], analgesic [7], antibacterial [8] and anticancer [9] agents. The majority of the ligands studied have either NS or NNS donor sequence. In comparison, complexes with ONS donor sequence are few in number. It is therefore of interest to synthesize complexes with such ligands which contain potential N,S and O as donor atoms. The synthesis, characterization and antibacterial activity of several N, S, O containing ligands and their metal complexes have been reported in this paper.

### Experimental

All chemicals used were reagent grade and were used as supplied by Merck except for ethanol which was purified by refluxing the 99% crude with magnesium turnings and iodine and finally distilled and stored.

**Physical measurement and elemental analyses.** IR spectra (as KBR pellets) were recorded on a Pye-Unicam SP3-300 IR spectrometer. Conductivities of  $10^{-3}$  M solution in dimethyl sulphoxide (DMSO) were measured at 25°C using a type CG857 No. 71798 Schott-Gerate, Germany, conductivity meter and dip-type cell with platinized electrodes. Magnetic measurement were performed by the Sherwood Scientific Magnetic Susceptibility Balance, London. Micro analyses for carbon, hydrogen and nitrogen were carried out by Regional sophisticated Instrumentation Centre, Lucknow, India. Sulphur contents were determined

by Carriou method [10].

**Antibacterial test.** The test organism *bacillus subtilis* from pure culture were taken in a nutrient broth and incubated at a temperature of 37°C for 24 hr. 1 ml of this culture was added to 100 ml of the sterile nutrient agar. A 25 ml portion of this mixer was poured into a petridish and rotated several times both clockwise and anticlockwise directions. The thickness of the medium was maintained to about 4 mm. After complete solidification of the medium, the sample discs were placed on the medium preceeded by the organism and the petridish was kept at 4°C for 24 hr. Then it was incubated for 12-24 hr. at 37°C. The inhibition was determined by measuring the diameter of the inhibition zone.

**Preparation of the ligands.** The ligands were prepared by the literature method [11] as follows:

2-Hydroxyphenylthiourea,  $C_7H_8N_2OS(L_1)$  : HCl (0.1 mole 36.5% HCl 10 ml) was added to 2-aminophenol (10.9g, 0.1 mole) which produced hydrochloride salt. The hydrochloride salt was added to  $NH_4SCN$  (7.6g 0.1 mole) and the mixture was heated in oil bath for 45 mins. at 120-130°C. 400 ml distilled water was added and stirred. The product was filtered and crystallized from acetone. TLC ( $CH_2Cl_2$ :Acetone = 10:1) of the reaction product clearly showed a single spot distinctly different from that of the reactant,  $R_f$  value = 60.2, yield = 83%, m.p. 161-162°C (literature [12] : 161°C). Anal. Found % : C, 49.95; H, 4.82; N, 16.59; S, 18.85; calc % for  $C_7H_8N_2OS$  : C, 49.98; H, 4.79; N, 16.65; S, 19.06.

Important IR bands in  $cm^{-1}$  (KBR pellets): 3345vs, 3320vs, 3060-3260br, 3090m, 1620s, 1610m, 1290s, 1200vs, 1080vs, 1040vs.

**4-Methylphenylthiourea,  $C_8H_{10}N_2S(L_2)$ :** p-Toluidine hydrochloride salt was added to appropriate amount of  $NH_4SCN$  and to it was added 500 ml distilled water. The mixture was refluxed to reduce the volume to ca 200 ml. The crystalline product was isolated and washed with ab. alcohol and recrystallized from acetone. Yield = 86%, M.P. = 189°C (Literature [13]: 188°C).

TLC ( $CH_2Cl_2$ : Acetone = 10:1),  $R_f$  value = 58.3, Anal. Found% : C, 57.64; H, 5.89; N, 17.00; S, 19.11; Calc (%) for  $C_8H_{10}N_2S$ : C, 57.80; H, 6.06; N, 16.85; S, 19.29.

Important IR bands in  $cm^{-1}$  (KBr pellets); 3450vs, 3280vs, 3160s, 3060s, 2885m, 1620vs, 1590s, 1078s, 1020vs.

**2-carboxyphenylthiourea,  $C_8H_8N_2O_2S(L_3)$ :** The same procedure as that for the ligand 2-hydroxyphenylthiourea was followed to prepare this ligand using anthranillic acid as the starting material. TLC ( $CH_2Cl_2$ : Acetone = 10:1),  $R_f$  value = 65.5 yield = 80% M.P. = 181°C Anal. Found (%) : C, 48.72; H, 4.08; N, 14.32; S, 16.45; Calc. for  $C_8H_8N_2O_2S$ : C, 48.97; H, 4.11; N, 14.28; S, 16.34.

Important IR bands in  $cm^{-1}$  (KBr pellets) : 3445vs, 3320v, 3040-3260br, 3090m, 1670s, 1610w, 1590vs, 1250vs, br, 1070m, 1030vs, 930vs.

**Preparation of the complexes.** General method for the preparation of complexes, 1-3: 0.01 mole of the ligand ( $L_1$ ) was dissolved in 30 ml ab. alcohol and 0.02 mole alcoholic

solution of KOH was added to it. The solution was then added to an alcoholic solution (20 ml) of the metal nitrate (0.01 mole). The mixture was warmed in water bath for few minutes. The resulting precipitate which separated out was filtered, washed several times with ab. alcohol and dried *in vacuo* over  $P_4O_{10}$ .

General method for the preparation of complexes, 4-6: 1.66 g (0.01 mole) of the ligand was dissolved in 40 ml. ab. alcohol and the solution was added to an alcoholic solution (30 ml) of the metal nitrate (0.005 mole). The mixture was warmed in water bath for half an hour. The precipitated complex was filtered and washed with ab. alcohol several times. The product was dried and stored as above. General method for the preparation of complexes, 7-9. The same procedure as that of 1-3 was followed for these complexes by using 1:1 mole ratio of the ligand, KOH and metal salt.

### Results and Discussion

The analytical data with other physical properties of the metal complexes are presented in Table 1. The conductivity data for solutions in DMSO indicate that the complexes 1, 2, 3 are all 2:1 electrolytes while 4-9 are non-electrolytes. The IR spectral data are shown in Table 2. The  $\nu NH_2$  bands of the free ligands are shifted to lower wave numbers upon complexation (1-9) indicating coordination by primary amino

TABLE I. ANALYTICAL DATA AND OTHER PHYSICAL PROPERTIES OF THE COMPLEXES<sup>a</sup>.

No. Compound	Colour	M.P. (°C)	% Metal calc. (Found)	% Carbon calc. (Found)	% Hydrogen calc. (Found)	% Nitrogen calc. (Found)	Molar conductance ( $W^{-1}cm^2mol^{-1}$ )	Magnetic moment (B.M.)
1. $K_2[Mn_2(L_1^{2-})_2(NO_3)_2]$	Grey	>250	18.26 (17.99)	26.05 (25.97)	1.87 (1.95)	13.02 (12.78)	55.50	4.13
2. $K_2[Co_2(L_1^{2-})_2(NO_3)_2]$	Black	>250	18.04 (18.25)	25.73 (25.59)	1.85 (1.63)	12.86 (12.65)	51.20	2.30
3. $K_2[Ni_2(L_1^{2-})_2(NO_3)_2]$	Black	>250	17.98 (17.79)	25.75 (26.00)	1.85 (1.83)	12.87 (13.00)	56.30	1.61
4. $[Mn(L_2)_2(NO_3)_2]$	Brown	>250	10.74 (10.85)	37.58 (37.39)	3.94 (4.05)	16.43 (16.35)	0.05	5.72
5. $[Co(L_2)_2(NO_3)_2]$	Reddish Black	>250	11.43 (11.30)	37.29 (37.27)	3.91 (3.72)	16.31 (16.52)	1.10	3.98
6. $[Ni(L_2)_2(NO_3)_2]$	Blackish	>250	11.40 (11.28)	39.30 (39.11)	3.91 (4.03)	16.31 (16.01)	0.90	2.99
7. $[Mn_2(L_3^-)_2(NO_3)_2]$	Brownish	>250	17.60 (17.45)	30.78 (30.69)	2.26 (2.07)	13.46 (13.25)	0.70	4.07
8. $[Co_2(L_3^-)_2(NO_3)_2]$	Grey	>250	18.64 (18.76)	30.39 (30.50)	2.23 (2.35)	13.29 (13.50)	0.90	2.18
9. $[Ni_2(L_3^-)_2(NO_3)_2]$	Ash	>250	18.58 (18.74)	30.41 (30.25)	2.23 (2.00)	13.30 (13.02)	0.00	1.54

<sup>a</sup>  $L_1^{2-}$  and  $L_3^-$  are deprotonated forms of the ligands 11 and 13 respectively.  $L_1$  = 2-Hydroxyphenylthiourea,  $L_2$  = 4-methylphenylthiourea,  $L_3$  = 2-Carboxyphenylthiourea. Molar conductance of ca  $10^{-3}$  solution in DMSO.

nitrogen[14] which is also supported by bands at 460-490 $\text{cm}^{-1}$  due to  $\nu(\text{M-n})$  modes [15,16]. The broad band at  $\sim 3260\text{-}3060\text{cm}^{-1}$  of the ligand  $L_1$  (2-hydroxyphenylthiourea) due to phenolic O-H, disappears upon complexation (1-3), suggesting deprotonation of the ligand. The coordination through phenolic oxygen atom is evident from the appearance of bands at 565-580  $\text{cm}^{-1}$  which are tentatively attributed to the  $\nu(\text{M-O})$  modes [15-17].

A further proof of bonding through the phenolic oxygen atom is the disappearance of the O-H deformation band (in plane) at 1290  $\text{cm}^{-1}$  in the complexes (1-3).

Complexes with 2-carboxyphenylthiourea (7-9) do not show O-H stretching modes suggesting deprotonation and coordination through the carboxylate oxygen atom. The shift of  $\nu_{\text{asy}}(\text{COO}^-)$  to higher frequency ( $\sim 1600\text{ cm}^{-1}$ ) and  $\nu_{\text{sym}}(\text{COO}^-)$  to lower frequency (1380-1360  $\text{cm}^{-1}$ ) confirm coordination through the carboxylate oxygen [18]. A further proof of bonding through the carboxylate anion is the disappearance of the O-H deformation band (out of plane) at 930 $\text{cm}^{-1}$  in the complexes. The M-O band is also present in the low frequency region at 255-270  $\text{cm}^{-1}$  in the complexes suggesting coordination through the carboxylate oxygen [19].

The IR spectra of all the complexes display bands characteristic of nitrate group ( $\sim 1390\text{ cm}^{-1}$ ,  $\sim 380\text{ cm}^{-1}$  and

$\sim 720\text{ cm}^{-1}$ ) [20,21]. The IR spectra of the ligands do not exhibit any peak attributable to the S-H around  $\text{ca } 2575\text{ cm}^{-1}$  indicating that in the solid state they remain in the thione form. The IR spectra of the ligands exhibit a band  $\text{ca } 1040\text{ cm}^{-1}$  (vs), 1020  $\text{cm}^{-1}$ (vs) and 1030  $\text{cm}^{-1}$ (vs) which may be assigned to the C = S stretching modes of the ligand  $L_1$ ,  $L_2$  and  $L_3$  respectively. A similar band 1045  $\text{cm}^{-1}$  (vs) in the IR spectra of S-benzylthiocarbamate,  $\text{NH}_2\text{NSCSSCH}_2\text{C}_6\text{H}_5$  was assigned to the C = S stretching mode [22].

The C=S stretching mode (1040  $\text{cm}^{-1}$ ) of the ligand,  $L_1$  disappears in the spectra of the metal complexes (1-3) suggests that the metal is coordinated with the deprotonated thiol form. Coordination of deprotonated thiol is supported by the appearance of a new band 640-650 $\text{cm}^{-1}$  assigned to  $\nu(\text{C-S})$  stretching [23,24]. The C = N stretching bands are also present at 1640  $\text{cm}^{-1}$  (s), 1640  $\text{cm}^{-1}$  (s) and 1660  $\text{cm}^{-1}$  (s) in the spectra of the complexes 1,2,3 respectively confirming the coordination through deprotonated thiol group. This is also evident from the appearance of band at 355-370  $\text{cm}^{-1}$  in these complexes which are tentatively attributed to the  $\nu(\text{M-S})$  modes [17,22,25]. In the complexes 7-9, the C = S stretch are shifted by  $\sim 60\text{-}70\text{ cm}^{-1}$  to lower wave numbers indicating coordination through thioketo sulphur atom, not thiol sulphur atom as is evident from the absence of C = N and C-S peaks

TABLE 2. IR SPECTRAL DATA FOR THE Mn(II), Co(II) AND Ni(II) COMPLEXES<sup>b</sup> (BAND/GROUP MAXIMA IN  $\text{cm}^{-1}$ ).

No.	Compounds	$\nu\text{NH}_2$	$\nu(\text{C=N})$	$\text{NO}_3$	$\nu(\text{C=S})$	$\nu(\text{C-S})$	$\nu(\text{M-O})$	$\nu(\text{M-N})$	$\nu(\text{M-S})$
	$\text{C}_7\text{H}_8\text{N}_2\text{OS}(\text{L}_1)$	3445vs 3320vs	-	-	1040vs	-	-	-	-
	$\text{C}_8\text{H}_9\text{N}_2\text{S}(\text{L}_2)$	3450vs 3280vs	-	-	1020vs	-	-	-	-
	$\text{C}_8\text{H}_8\text{N}_2\text{O}_2\text{S}(\text{L}_3)$	3445vs 3320vs	-	-	1030vs	-	-	-	-
1.	$\text{K}_2[\text{Mn}_2(\text{L}_1^{2-})_2(\text{NO}_3)_2]$	3410w 3240w	1640s	1385vs	-	650s	565m	490w	365w
2.	$\text{K}_2[\text{Co}_2(\text{L}_1^{2-})_2(\text{NO}_3)_2]$	3380w 3300w	1640s	1390vs	-	640m	580m	480w	370m
3.	$\text{K}_2[\text{Ni}_2(\text{L}_1^{2-})_2(\text{NO}_3)_2]$	3400w 3290w	1660s	1380vs	-	640s	575w	485m	485m
4.	$[\text{Mn}(\text{L}_2)_2(\text{NO}_3)_2]$	3400m 3220m	-	1375vs	-	-	-	475w	-
5.	$[\text{Co}(\text{L}_2)_2(\text{NO}_3)_2]$	3350w 3225w	-	1382vs	-	-	-	485m	-
6.	$[\text{Ni}(\text{L}_2)_2(\text{NO}_3)_2]$	3380m 3230m	-	1385vs	-	-	-	460w	-
7.	$[\text{Mn}_2(\text{L}_3^-)_2(\text{NO}_3)_2]$	3340m 3260m	-	1380vs	970m	-	280m	490w	380w
8.	$[\text{Co}_2(\text{L}_3^-)_2(\text{NO}_3)_2]$	3360w 3230w	-	1400vs	960m	-	255m	490w	380w
9.	$[\text{Ni}_2(\text{L}_3^-)_2(\text{NO}_3)_2]$	3350m 3240m	-	1405	965m	-	270m	490m	385m

<sup>b</sup> Relative band intensities are denoted by vs, s, m and w i.e. very strong, strong, medium and weak respectively.

TABLE 3. ANTIBACTERIAL ACTIVITY OF THE LIGAND AND THEIR COMPLEXES.

Complex No.	Ligands and complexes	Activity*
	L <sub>1</sub>	+++
	L <sub>2</sub>	++
	L <sub>3</sub>	+
1.	K <sub>2</sub> [Mn <sub>2</sub> (L <sub>1</sub> <sup>2-</sup> ) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> ]	-
2.	K <sub>2</sub> [Co <sub>2</sub> L <sub>1</sub> <sup>2-</sup> ) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> ]	+++
3.	K <sub>2</sub> [Ni <sub>2</sub> (L <sub>1</sub> <sup>2-</sup> ) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> ]	+++
4.	[Mn(L <sub>2</sub> ) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> ]	+++
5.	[Co(L <sub>2</sub> ) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> ]	+++
6.	[Ni(L <sub>2</sub> ) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> ]	+++
7.	[Mn <sub>2</sub> (L <sub>3</sub> <sup>-</sup> ) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> ]	-
8.	[Co <sub>2</sub> (L <sub>3</sub> <sup>-</sup> ) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> ]	-
9.	[Ni <sub>2</sub> (L <sub>3</sub> <sup>-</sup> ) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> ]	+

+++,,+,+ indicates strong, medium, and weak inhibition respectively; - indicates no inhibition. \* Activity tested with *Bacillus subtilis*.

in the spectra. The metal-sulphur [17,22,25] band also present at 350-385 cm<sup>-1</sup> which supports coordination through the sulphur atom.

The metal complexes 4, 5 and 6 (with 4-methylphenylthiourea) display room temperature magnetic moment values of 5.72, 3.98 and 2.99 B.M. corresponding to 5, 3 and 2 unpaired electrons respectively indicating a tetrahedral geometry for these complexes. The complexes 1-3 (with 2-hydroxyphenylthiourea) on the other hand, shows magnetic moment values of 4, 13, 2.30 and 1.61 B.M. respectively. The low magnetic moment values for the later complexes are presumably due to the presence of antiferromagnetic interaction between a pair of metal ions involving oxygen or sulphur bridging dimeric structure [26,27]. The same type of magnetic behaviour is also observed for the complexes with 2-carboxyphenylthiourea again suggesting structural similarities between the complexes of 2-hydroxyphenylthiourea and 2-carboxyphenylthiourea. The shift of C-O stretching band toward higher frequencies, relative to the mononuclear complexes also indicates that bridging C-O group is present in these complexes. The low magnetic moment, molar conductance, IR spectral studies and elemental analyses of the complexes 1-3 and 7-9 are in favour of a 5-coordinate bridging structure [28]. The normal magnetic moment, IR spectral studies, molar conductance and elemental analyses of the complexes 4-6 support 4-coordinate tetrahedral structures.

Many ligands and their metal complexes are known [29,30] to have antibacterial activity. The antibacterial activity of the ligands (L<sub>1</sub>, L<sub>2</sub>, L<sub>3</sub>) and their complexes (Table 3) with *Bacillus subtilis* was determined by Agar Diffusion method. The ligands, 2-hydroxyphenylthiourea (L<sub>1</sub>) is not bactericidal towards *Bacillus subtilis*, i.e. bacteriostatic. The complexes of this ligand 2 and 3 have been found to be strongly active

but 1 shows no inhibitory action against the same microorganism. The ligand, 4-methylphenylthiourea (L<sub>2</sub>) display medium inhibition towards *Bacillus subtilis*, but its complexes, 4,5 and 6 show strong inhibition. The ligand, 2-carboxyphenyl-thiourea (L<sub>3</sub>) has been found to possess slight inhibitory effect and its complexes 7,8 show no inhibition whereas 9 retains the same activity as that of the free ligand.

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