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Synthesis,Characterisation and Structural Studies on Metal Complexes Derived from Benzofuran Thiosemicarbazide Ligands and their Antimicrobial Activities

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ABSTRACT

The complexes of the type MLXn where M=Co(III),Fe(III), Mn(III), Ti(III),V(III), Ru(III),Ru(II) MoO(V),MoO_2(VI) and UO_2(VI),X=Cl/NO_3, n=2/4, and L is the thiosemicarbazide ligand derived from reaction between benzofuran-2-carboxy hydrazide and phenylisothiocyanate(BCPT)were prepared. All the complexes isolated in solid state, are stable in air and characterized by the elemental analyses, IR, electronic spectral data, magnetic moment and conductance measurement studies. Thiosemicarbazide ligand behaves as bidentate by co-ordinating through oxygen of carbonyl group and nitrogen of hydrazine residue. The probable structure for all the metal complexes are also proposed here. The thiosemicarbazide ligand and its metal complexes have been screened for their antimicrobial activity.

Key words: Benzofuran,thiosemicarbazide, antimicrobial activity, ligand, octahedral.

INTRODUCTION

Thiosemicarbazides are important compounds because of their reported industrial and biological activities like anticonvulsant, antifungal plant growth promoting and antibacterial activity. Thiosemicarbazides are also used as intermediates for the synthesis of heterocyclic compounds such as 1,2,4triazoles,1,3,4, thiadiazoles and 1,3,4-oxadiazoles derivatives. A general method for the synthesis of thiosemicarbazides is the condenstion of isothiocyanate and derivatives of the carboxylic acid hydrazides in ethanol as solvent under reflux[1].

Thiosemicarbazide and thiosemicarbazone possess various important biological activities.The complexes of thiosemicarbazides and their thiosemicarbazones have been reported in literature[2].

Thiosemicarbazones and their complexes exhibit a great variety of biological activity. In recent years, thiosemicarbazones have been used for the analytical determination of metals. The chelation behaviour and electronic properties of aromatic and aliphatic thiosemicarbazones obtained by organic moieties with biological interest has been studied[3].

The complexes of thiosemicarbazides and their thiosemicarbazones have been reported in literature. Various types of ligands containing thiosemicarbazone moieties have been prepared and their complexation behaviour studied.

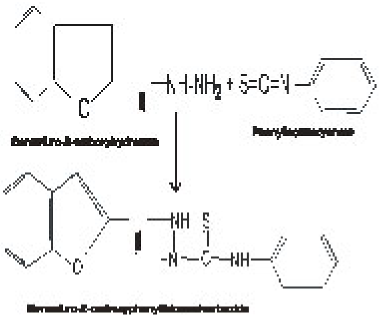
EXPERIMENTAL

All the chemicals and reagent used were of highest purity or A. R. grade. The compound benzofuran-2-carboxyhydrazide was prepared by the literature method[4]. The metal and chloride contents were determined as already reported[5]. The carbon,hydrogen and sulphur content in each sample were measured on perkin-Elmer (2400) CHNS analyzer. The UV-vis spectra of the complexes were recorded on a Shimadzu UV-1601 spectrophotometer.

Magnetic susceptibility measurements of complexes were carried out using a Gouy's balance at room temperature and Hg[Co(SCN)4] as calibrant. Molar conductivity was measured on an Elico CM180 conductivity meter with a dip-type cell using 10-3M solution of complexes in DMF.

Preparation of benzofuro-2-Carboxy- Phenyl thiosemicarbazide

The phenyl-isothiocyanate(0.5)mol in alcohol(10ml) was added to an ethanolic(20ml) solution of benzofuran-2-carboxyhydrazide (1.7g,0.5mol)with stirring. The reaction mixture was refluxed on water bath for about 4h. The solid thiosemicarbazide started separating after a few minutes. The product was filtered out and washed with alcohol. The compound was crystallized from alcohol and dried in vacuum over fused $CaCl_2$. The purity of sample was tested by TLC. [Mol. Formula $C_{16}H_{13}N_3O_2S$, m.p=260°C



RESULTS AND DISCUSSION

The elemental analyses show 1:2 (metal : ligand) stoichiometry for all the complexes. The analytical data of the ligand and the complexes are given in table 1. It corresponds well with the general formula $[M(C_{16}H_{13}N_3O_2S)_2]X$.where M= Ti(III), Ru(III), Ru(II),Mn(III),Fe(III),Co(III),V(III), MoO(V),MoO_2(VI) UO_2 (VI),X=Cl- for Ti(III), Ru(III), Mn(III), Fe(III) Co(III), V(III), MoO(V), MoO2(VI) for UO_2(VI), X =NO_3^- and Ru(II) X=Zero.

I.R. Spectra

The thiosemicarbazide ligand exhibits three bands at 3441, 3365 and 3130cm^{-1} assigned to $\upsilon(^4NH)$, $\upsilon(^2NH)$and $\upsilon(^1NH)$, respectively, in view of the earlier reports. In the spectra of the complexes, the bands due to (4NH) shifts to higher wave number side by about 10cm^{-1} and in some complexes it remains unaltered indicating non-involvement of nitrogen of $\upsilon(^4NH)$ group in co-ordination with metal ions. The band due to $\nu(^2NH)$ shift to lower wave number side by about 20-30cm^{-1} in all the complexes and this band becomes weak in the complexes suggesting the co-ordination of nitrogen of $\upsilon(^2NH)$ group. The bands observed in the region 3130cm^{-1} remains practically unaltered or shifts slightly to higher side indicating no co-ordination.

The weak band observed at 2780 cm^{-1} is assigned to stretching vibrations of intramolecular hydrogen bonding between CO and ^2NH group. The absence of any band above 3500 cm^{-1} due to $\nu(OH)$ and 2600-2500cm^{-1} due to $\nu(SH)$ suggests that ligand exists in thioketo form.

The strong bands observed at 1659 and 1675cm^{-1} in free ligand are assigned to $\upsilon(CO)$ vibrations. These bands shift to lower wave number side by about 30-50cm^{-1} in all the metal complexes. This suggests the co-ordination of oxygen with metal ions. The positive shift of $\upsilon(N\text{-}N)$ bands observed at 1010cm^{-1} in free ligand is shifted to higher wave number side by 10-15cm^{-1} in the complexes thereby showing the co-ordination of one of the nitrogen atom of hydrazinic moiety in bonding.

The thioketo $\nu(C{=}S)$ band observed at 737cm^{-1} shows no shift in the metal complexes as compared with free ligand. This shows sulphur atom of (C=S) has not taken part in co-ordination. The thioamide bands observed at 1540,1360,1080 and 740cm^{-1} due to amide I,II,III,IV,respectively, remain unaltered or do not show considerable change in the complexes suggesting the non involvement of(C=S) group in bonding with metal ions.

In UO_2complex, bands at 910 and 930 cm^{-1} indicated linear character of UO_2 group.

In the far infrared spectra of the complexes, the bands observed in the region 560-485cm^{-1} can be assigned to ν(M-N) vibrations and bands in the region 475-425cm^{-1} are assigned to (M-O) vibrations in all the complexes. The (M-Cl) band has appeared in the range of 325-360 cm^{-1}.

In case of oxomolybdenum(V)complex the band at 950cm^{-1} may be assigned to Mo=O moiety.

In dioxomolybdenum(VI)complex the bands at 960 & 910cm^{-1}. These bands indicated cis character of O=Mo=O moiety.

Magnetic Moment and Electronic Absorption Spectra

The Ti(III) complex shows magnetic moment of 1.73 B.M. This value is closed to the calculated value for d^1 system (1.73B.M.) like Ti(III) and show paramagnetic character for the complex. The electronic spectrum of the complex shows a single band at 19600cm^{-1},which may be assigned to $^2T_{2g}\rightarrow{}^2E_g$ transition[6]. This is characteristic of Ti(III) octahedral complex.

The magnetic moment of the vanadium(III) complex is 2.91 B.M.which is nearly equal to the calculated value for d^2 system like V(III). The electronic specrum of V(III) complex exhibited band at 16200cm^{-1} and shoulder at 20800cm^{-1}. The low energy band may be assigned to the $^3T_{1g}(f)\rightarrow{}^3T_{2g}(f)$. transition in octahedral symmetry, and high energy band to $^3T_{1g}(f)\rightarrow{}^3T_{1g}(p)$ transition[7].

The magnetic moment of Ru(III) complex is 1.82B.M. The electronic spectrum shows bands at 10330,16129,24390 and 35087cm^{-1} may be assigned to the transition $^2T_{2g}\rightarrow{}^4T_{1g}$, $^2T_{2g}\rightarrow{}^4T_{2g}$, $^2T_{2g}\rightarrow{}^2A_{2g}$,$^2T_{1g}$ and $\pi\rightarrow T_{2g}(\pi^*)$ levels respectively[8]. These are characteristic of an octahedral geometry.

The Ru(II)complex is diamagnetic in nature. The electronic spectrum of the complex in CH_2Cl_2 shows a band assigned to the charge transfer transition arising from the excitation of an electron from the metal t_{2g} level to the unfilled molecular orbitals derived from the π^* level of the ligand in accordance with the assignments made for other similar octahedral ruthenium(II) complex[9-11].

The magnetic moment of Mn(III)complex is 4.90 B.M. which is in expected range for d^4 system like Mn(III) and suggested paramagnetic nature for the complex and revealed high spin nature of the complex. It supported octahedral symmetry[12]. Unusually Mn(III) has ^5D electronic ground state and in an octahedral symmetry,a single absorption band is expected due to spin allowed transitions $^5E_g\rightarrow{}^5T_{2g}$ however even for symmetrical ligand field, they are subject to Jahn-Teller distortion for high spin d^4 configuration[13].

The complex shows two bands assignable to $^5B_{1g}\rightarrow{}^5T_{2g}$ at 18500cm^{-1} transition[14] and other band at 25000cm^{-1} may be assigned to Mn(dπ)$\rightarrow\pi^*$(azomethine)[14].

The magnetic moment of Fe(III) complex is 5.97 B.M.corresponding to five unpaired electron and high spin state of Fe(III) ion. Three bands have been observed in the electronic spectrum of the complex at 11235,21740 and 27780cm^{-1} assignable to $^6A_{1g}\rightarrow{}^4T_{1g}$, $^6A_{1g}\rightarrow{}^4T_{2g}$ and $^6A_{1g}\rightarrow{}^4E_g$ transitions respectively suggesting an octahedral geometry[15].

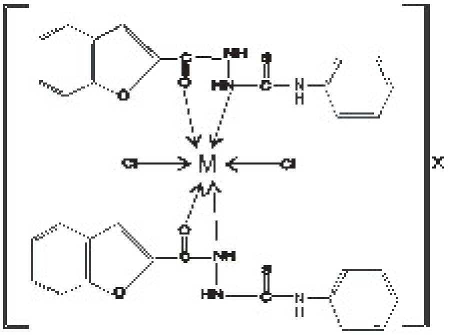
The magnetic study of Co(III)complex indicated diamagnetic nature for the complex, as expected for low spin d^6 ion.

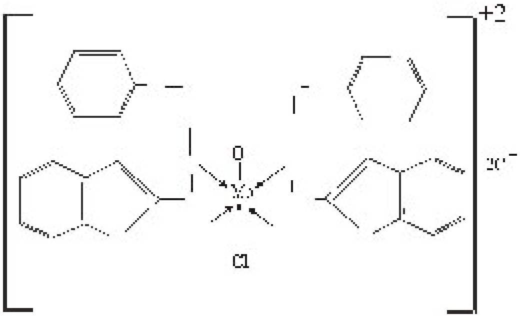
The electronic spectrum shows bands at 15140, 21110 and 23330cm^{-1}. These bands have been assigned to $^1A_{1g}\rightarrow{}^3T_{2g}$,$^1A_{1g}\rightarrow{}^1T_{1g}$ and $^1A_{1g}\rightarrow{}^1T_{2g}$. transitions respectively[16].

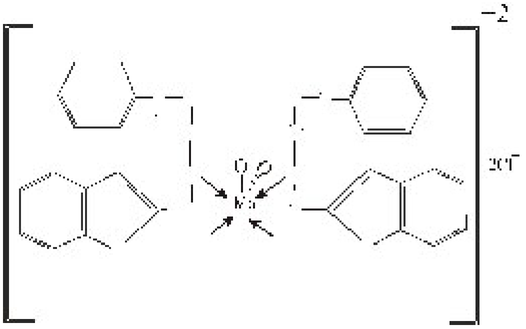
The magnetic moment of MoO(V)complex is 1.70B.M. which is very near to calculated value for one unpaired electron. The electronic spectrum shows bands at 14200,19610 and 25000cm^{-1} which

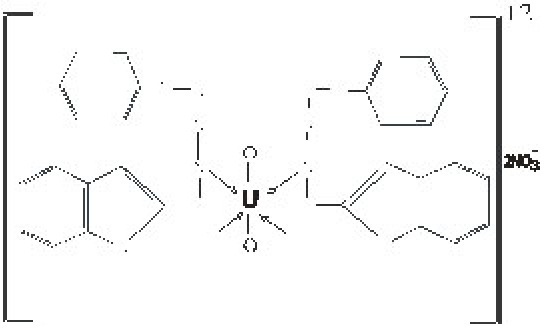
Table 1: Characterisation of metal complexes (obs.values).

S.NO.	**Complexes & Molecular wt.**	**Colour**	**M.P. ^0C**	**Elemental Analyses**						**Mag. Moment**	**Molar-conductance Ohm^{-1} cm^2 mol^{-1}**	
				%C	**%H**	**%N**	**%S**	**%Cl**	**%M**	**B.M.**	**DMF**	**Electrolyte Type**
1	[Ti($C_{16}H_{13}N_3O_2S$)$_2$.Cl_2]Cl Mol. For. Wt.=776.5	Yellow	310	49.39 (49.45)	3.31 (3.34)	10.71 (10.81)	8.21 (8.24)	13.67 (13.71)	6.13 (6.18)	1.73	56	1:1
2	[Ru($C_{16}H_{13}N_3O_2S$)$_2$.Cl_2]Cl Mol. For. Wt.=829.5	Green	331	46.23 (46.29)	3.09 (3.13)	10.08 (10.12)	7.68 (7.71)	12.77 (12.83)	12.14 (12.17)	1.82	61	1:1
3	[Ru($C_{16}H_{13}N_3O_2S$)$_2$.Cl_2] Mol. For. Wt.=794	Black	328	48.31 (48.36)	3.23 (3.27)	10.51 (10.57)	8.04 (8.06)	8.89 (8.94)	12.67 (12.72)	Diamag netic	----	Non electrolyte
4	[V($C_{16}H_{13}N_3O_2S$)$_2$.Cl_2]Cl Mol. For. Wt.=779.5	Light Yellow	314	49.21 (49.26)	3.29 (3.33)	10.66 (10.77)	8.17 (8.21)	13.61 (13.66)	6.49 (6.54)	2.91	56	1:1
5	[Mn($C_{16}H_{13}N_3O_2S$)$_2$.Cl_2]Cl Mol. For. Wt.=783.5	Dark Brown	312	48.96 (49.01)	3.27 (3.31)	10.69 (10.72)	8.11 (8.16)	13.52 (13.59)	6.96 (7.01)	4.90	60	1:1
6	[Fe($C_{16}H_{13}N_3O_2S$)$_2$.Cl_2]Cl Mol. For. Wt.=784.5	Brown	306	48.91 (48.94)	3.28 (3.31)	10.66 (10.70)	8.11 (8.15)	13.51 (13.57)	7.09 (7.13)	5.97	62	1:1
7	[Co($C_{16}H_{13}N_3O_2S$)$_2$.Cl_2]Cl Mol. For. Wt.=787.5	Pink	315	48.71 (48.76)	3.25 (3.30)	10.61 (10.66)	8.08 (8.12)	13.47 (13.52)	7.42 (7.49)	Diamag netic	69	1:1
8	[MoO($C_{16}H_{13}N_3O_2S$)$_2$Cl]Cl_2 Mol. For. Wt.=840.5	Light Yellow	335	45.62 (45.68)	3.02 (3.09)	9.92 (9.99)	7.57 (7.61)	12.61 (12.67)	11.39 (11.42)	1.70	107	1:2
9	[MoO_2($C_{16}H_{13}N_3O_2S$)$_2$]Cl_2 Mol. For. Wt.=821	White	342	46.72 (46.77)	3.12 (3.16)	10.17 (10.23)	7.72 (7.79)	8.59 (8.64)	11.62 (11.79)	Diamag netic	115	1:2
10	[UO_2($C_{16}H_{13}N_3O_2S$)$_2$]2NO_3 Mol. For. Wt.=1016	Creamish White	372	37.71 (37.79)	2.48 (2.55)	11.00 (11.02)	6.25 (6.29)	—	23.36 (23.42)	Diamag netic	110	1:2









have been assigned to $^{2}B_{2}\rightarrow{}^{2}E$(dxy→dxz-dyz), $^{2}B_{2}\rightarrow{}_{2}B_{1}$(dxy→dx2-y2) and $^{2}B_{2}\rightarrow{}^{2}A1$ (dxy→dz^{2}) transitions respectively[17].The complex can be best considered as octahedral with strong tetragonal distortion(C_{4r} symmety)resultig from Mo=O bond[18].

The electronic spectrum of MoO_2(VI) complex shows only charge transfer band.

CONCLUSION

Based on the studies performed an octahedral geometry has been proposed for all the synthesised complexes.

Where M=Ti(III),Ru (III), Ru(II),Mn(III), Fe(III), Co(III), V(III) where X=Cl For Ti(III),Ru (III), Mn(III), Fe(III),Co(III),V(III)except. Ru(II).

In case of MoO(V),MoO_2(VI),UO (VI) complexs show octahedral geometry as given below.

Antimicrobial activity

All the metal complexes, ligand and metal salts were tested for their antimicrobial activity against bacteria *E.coli, Pseudomonas, B.substilis* and wild bacillus by cup-plate zone inhibition technique at the concentrations of 1mg/ml in DMF solution. The standard used was gentamycine sulphate 20mg/ml and solvent control was also put to know the activity of the solvent.

The Fe(III),UO_2(VI), MoO(V),MoO_2(VI) and V(III) complexes show a significant inhibition of growth of activity against Pseudomonas and wild bacillus bacteria, respectively, as compared to the ligand and metal ions. The ligand benzofuro-2-carboxy phenylthiosemicarbazide did not show any inhibition against any bacteria. All other complexes have shown less inhibition against all bacteria tested. These preliminary results suggest that the activity of ligand is changed when it is presented in the form of metal complexes.

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