

Synthesis, characterisation of complexes derived from physiologically active transition metals

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ABSTRACT

A few complexes of the ligand N-benzoyl-N-p-hydroxythio- benzhydrazine with the metals titanium(III), vanadium (III), Iron(II) & (III) and Oxomolybdenum(V) having the composition $[M(HBptbh)_2(H_2O)_2]$ have been prepared and characterised by elemental analyses, IR & electronic spectra, molar conductance and magnetic susceptibility. These studies suggested octahedral geometry around the respective metal ions. The ligands and their corresponding complexes were also screened for their biological activities.

Key words: Transition metals complexes, synthesis, biological activity

INTRODUCTION

The inorganic complexes based materials that exhibit unusual solid state properties has become a field of dramatic growth. Some sulphur and nitrogen containing ligands and their corresponding metal complexes have been found to possess semi conductor properties¹, and have been used as photosensitizer for conversion of light energy into electricity. Few reports have appeared on 3d metal complexes of p-hydroxythiohydrazine^{2,3} and its N-aryl derivatives⁴.

Titanium, vanadium and molybdenum possess a number of oxidation states and have excellent complexing property. The last two metals and their complexes exhibit biological properties. Keeping in view these facts we have synthesised ligands having oxygen, nitrogen and sulphur donors and studied their structures.

MATERIAL AND METHODS

All the chemicals used were of AR grade or equivalent purity. The chemicals used for the preparation of the ligand were benzoic acid hydrazide ammonium polysulphide and carboxy methyl-p-hydroxydithiobenzoate were prepared by the method in the chemical literature⁽⁵⁻⁸⁾. Titanium(III) chloride was prepared in the lab from 12% solution of Ti(III) chloride (B.D.H) by the reported method. All other metal salts were purchased from the market and used as such.

Preparation of H₂Bptbh

It was prepared by refluxing the alkaline solutions of benzoic acid hydrazide and carboxy methyl-p-hydroxydithiobenzoate, each dissolved in 0.5 N-NaOH. To this reaction mixture was added dropwise dilute acetic acid. The solution was allowed to stand for about two hrs. The precipitated ligand was filtered, washed with water and recrystallised from hot ethanol, mp. 127°C.

Preparation of complexes

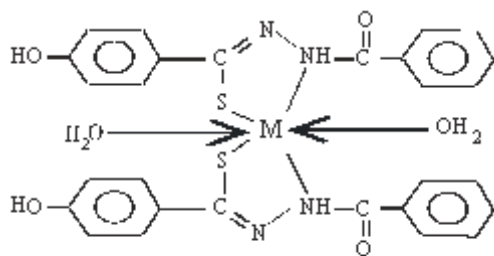
The complexes were prepared by refluxing the ethanolic solution of the metal salt with the solution of the ligand for about 1hr. The precipitated complexes were filtered, washed and dried in vacuo.

RESULTS AND DISCUSSION

The vast difference in melting points of the ligand and its corresponding metal complexes indicated their formation. Elemental analyses for C,H,N and gravimetric estimation of the metal indicated 1:2 M:L stoichiometry for all the complexes. On this basis various complexes may be formulated as $[M(\text{HBptbh})_2 \cdot 2\text{H}_2\text{O}]$. These complexes were formed by the loss of one proton from each ligand molecule. All the complexes were found to be insoluble in acetonitrile, water, methanol and chloroform, but soluble in DMSO and DMF.

The molar conductance values in both DMSO and DMF indicated 1:2 electrolytic nature for titanium(III), vanadium(III), Iron(III), Mo(V) complexes where as Fe(II) complex was 1:1 electrolyte.

The IR spectrum of the ligand and the complexes were recorded in KBr phase. The IR



[M-Ti(III), V(III), Fe(III), Fe(II)]

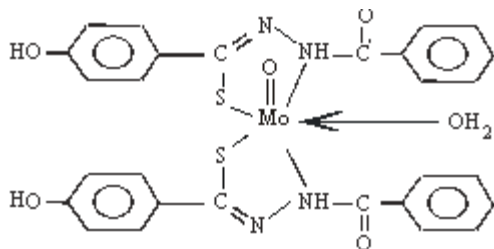


Table 1: Analytical and Physical data of the complexes

S. No.	Complexes and Molecular formula	Colour	Mol wt	m.p. °C	Elemental Analysis					Mag.		Molar-conductance	
					%C	%H	%N	%S	CI	%M	B.M.	DMF	DMSO
1.	$[\text{Ti}(\text{HBptbh})_2(\text{H}_2\text{O})_2]\text{Cl}_2$	Yellow	797	180	42.15 (41.90)	2.76 (2.45)	7.02 (6.98)	16.0 (15.85)	8.90 (8.78)	6.02 (5.97)	1.71	190	89
2.	$[\text{V}(\text{HBptbh})_2(\text{H}_2\text{O})_2]\text{Cl}_2$	Light yellow	800	162	42.00 (41.81)	2.75 (2.69)	7.00 (6.89)	16.00 (15.84)	8.87 (8.58)	6.37 (6.19)	2.90	186	91
3.	$[\text{Fe}(\text{HBptbh})_2(\text{H}_2\text{O})_2]\text{Cl}_2$	Reddish yellow	806	179	40.82 (40.82)	2.55 (2.38)	6.94 (6.89)	15.8 (15.69)	8.80 (8.66)	6.94 (6.71)	5.90	180	85
4.	$[\text{Fe}(\text{HBptbh})_2(\text{H}_2\text{O})_2]\text{Cl}$	Pale yellow	771	146	43.50 (42.90)	2.85 (2.78)	7.26 (7.15)	16.60 (16.51)	4.66 (4.52)	7.65 (7.5)	4.89	106	57
5.	$[\text{MoO}(\text{HBptbh})_2(\text{HO})_2]\text{Cl}_2$	Brown	826	192	40.67 (40.10)	2.66 (2.51)	6.77 (6.58)	15.49 (15.10)	8.59 (8.46)	11.62 (11.31)	1.75	189	90

Value in brackets are observed values

spectra of the ligand shows bands at 3360 and 3300 cm^{-1} due to the presence of two NH groups. A band also appears at 3280 cm^{-1} due to νOH of the ligand⁹. The bands at 1635, 1450, 1375, 885 and 1000 cm^{-1} have been assigned to $\nu(\text{C}=\text{O})$, thioamide I, $[(\text{NH}+\nu(\text{CN}))]$, thioamide II $[\nu(\text{CN})+\beta(\text{NH})]$, $\nu(\text{C}=\text{S})$ and $\nu(\text{N}-\text{N})$ modes respectively⁽¹⁰⁾. In the IR spectra of the complexes, the presence of a band in the range of 3305-3325 cm^{-1} due to $\delta(\text{NH})$, suggested the loss of one NH proton via thioenolisation. The ligand band at 1635 cm^{-1} appeared unchanged in the IR spectra of the complexes, suggesting non-involvement of carbonyl oxygen in bonding. The $\nu\text{C}=\text{S}$ was found to be absent in the IR spectra of the complexes but a new band due to $\nu(\text{C}-\text{S})$ appeared in the spectra of the complexes suggesting bonding through this group¹⁰. The positive shift in the band due to $\nu(\text{N}-\text{N})$ suggested bonding through one hydrazinic nitrogen. Thus the ligand is behaving in uninegative bidentate manner.

The appearance of non ligand band in the IR spectra of all the complexes in the range of 3380-3400 cm^{-1} indicated the presence of water molecules. The OH rocking and wagging bands in the range of 800-720 cm^{-1} indicated their coordinated nature. Thermogravimetric analysis of the complexes also confirmed the inference of IR spectra regarding co-ordinating nature of the water molecules. A strong band appearing at 950 cm^{-1} in the oxomolybdenum(V) complexes has been attributed to $\nu(\text{M}=\text{O})(\text{II})$.

The magnetic susceptibility of the complexes was determined by Gouys method. From the value of the magnetic susceptibility the value of magnetic moments was calculated. The values for the various metal complexes are given in the table 1. These values indicated that all the studied complexes are paramagnetic in nature. The values also suggested octahedral geometry around Ti^{+3} , V^{+3} , Fe^{+2} , Fe^{+3} , and MoO^{+3} metal ions.

The electronic spectra of the complexes were recorded. The electronic spectrum of $\text{Ti}(\text{III})$ complex exhibits a single broad band at 19230 cm^{-1} which may be due to the transition ${}^2\text{T}_{2g} \rightarrow {}^2\text{E}_g$ for octahedral geometry¹². For $\text{Fe}(\text{III})$ Complex, three bands at 12300, 21700 and 27500 cm^{-1} have been

observed. These bands may be due to ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{1g}$, ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{2g}$ and ${}^6\text{A}_{1g} \rightarrow {}^4\text{E}_g$ transitions respectively¹³, which are characteristic of octahedral geometry. The electronic spectra of the $\text{V}(\text{III})$ complex is indicative of octahedral geometry. The spectrum exhibited bands at 16600 cm^{-1} and 21700 cm^{-1} , which have been assigned to ${}^3\text{T}_{1g} \rightarrow {}^2\text{T}_{2g}(\text{P})$ and ${}^3\text{T}_{1g} \rightarrow {}^3\text{T}_{2g}$ transitions respectively.

The electronic spectrum of $\text{Mo}(\text{V})$ complex exhibits three absorption bands in the ligand field region. The low intensity band may be due to first crystal field transition ${}^2\text{B}_2 \rightarrow {}^2\text{E}$ ($d_{xy} \rightarrow d_{xz}, d_{yz}$). This transition was observed at 13500 cm^{-1} . The second CF transition was observed at 19700 cm^{-1} which may be due ${}^2\text{B}_2 \rightarrow {}^2\text{B}_1$ ($d_{xy} \rightarrow d_{x^2-y^2}$). The third peak was observed at 25500 cm^{-1} and is due ${}^2\text{B}_2 \rightarrow {}^2\text{A}_1$ ($d_{xy} \rightarrow d_{z^2}$)¹⁴. These are characteristic of octahedral geometry.

The μ_{eff} value of 4.90 B.M. is in good agreement with that of the reported value for octahedral $\text{Fe}(\text{II})$ complexes. Electronic spectral bands at 10500, 31400 and 40600 cm^{-1} are attributed to ${}^5\text{T}_{2g}(\text{D}) \rightarrow {}^5\text{E}_g(\text{D})$, ${}^5\text{T}_{2g}(\text{D}) \rightarrow {}^3\text{T}_{1g}(\text{H})$ and ${}^5\text{T}_{2g}(\text{D}) \rightarrow {}^3\text{E}_g(\text{H})$ transitions respectively. These transition are spin forbidden and are possibly due to $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions of the ligand. The Dq value is very close to that for octahedral $\text{Fe}(\text{II})$ complexes¹⁵.

In view of the results of these studies all the reported complexes seems to have octahedral geometry with the exception $\text{MoO}(\text{V})$ complex, which seems to have some distortion due to $\text{Mo}=\text{O}$ moiety.

Biological activity

The biological activities of ligand and their corresponding metal complexes were tested against several bacteria and fungi at 200 $\mu\text{g ml}^{-1}$. The studies revealed that the complexes exhibited higher antibacterial and antifungal properties than the corresponding ligands. The order of the activity of various metal complexes was $\text{Mo} > \text{V} > \text{Ti}$.

The ligand showed antibacterial activity against both aureus and *S typhi* with MIC value 20 $\mu\text{g ml}^{-1}$. The metal complexes of V & Ti exhibited higher antibacterial activity against both, but the Mo

complex showed a MIC value of $40\mu\text{g}\cdot\text{ml}^{-1}$ against these microorganisms.

The ligand showed antifungal activity

against candida albicans, T rubrum with MIC value of $200\mu\text{g}\cdot\text{ml}^{-1}$ where as the metal complexes were found to be more protent than the ligand.

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