



Studies on Polystyrene-Anchored Coordination Compounds of Divalent, Trivalent, Tetravalent and Hexavalent Metal Ions with the Schiff Base Obtained from the Condensation of 3-Formylsalicylic Acid and *o*-Hydroxyphenylurea

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Chloromethylated polystyrene (PS-CH₂Cl) reacts with 3-formylsalicylic acid and forms polystyrene 3-formylsalicylate. The nucleophilic addition reaction followed by elimination of one water molecule between polystyrene-3-formylsalicylate and *o*-hydroxyphenylurea in DMF in the presence of ethyl acetate results in the formation of polystyrene-anchored Schiff base, PSCH₂-LH₃ (**1**). Polystyrene-anchored coordination compounds, [PSCH₂-LH₂M(OAc)(DMF)] (**2**) (where M = Cu, Co), [PSCH₂-LH₂M'(OAc)(DMF)] (**3**) (here M' = Zn, Cd), [PSCH₂-LH₂M''(OAc)(DMF)₃] (**4**) (M'' = Mn, Ni), [PSCH₂-LH₂FeCl₂(DMF)₂] (**5**), [PSCH₂-LH₂MoO₂(acac)] (**6**) (acacH = pentane-2,4-dione), [PSCH₂-LH₂Zr(OH)₃(DMF)₂] (**7**) and [PSCH₂-LH₂UO₂(OAc)(DMF)] (**8**) have been synthesized by refluxing a DMF swollen suspension of **1** and appropriate metal salts/compound. The polystyrene-anchored coordination compounds have been characterized on the basis of elemental analyses, spectral (IR, UV-VIS, ESR) and magnetic susceptibility measurement. **1** behaves as a monobasic bidentate ON donor ligand in these coordination compounds. [PSCH₂-LH₂M(OAc)(DMF)] (**2**) (M = Cu, Co) is square-planar and paramagnetic, [PSCH₂-LH₂M'(OAc)(DMF)] (**3**) (M' = Zn, Cd) is tetrahedral and diamagnetic. An octahedral geometry has been assigned to the paramagnetic compounds (**4** and **5**) and to the diamagnetic compounds (**6** and **8**). The coordination number of Zr is seven in **7**. A pentagonal-bipyramidal geometry has been assigned to the latter.

Key Words: Polymer-anchored, Azomethine linkage, Spectral studies, *o*-Hydroxyphenylurea.

INTRODUCTION

The functionalized polymers and their coordination compounds are known to exhibit the chelating abilities¹, catalytic activity^{2,3} selectivity, efficiency, operational flexibility and stability^{4,5}. A perusal of the literature indicates that a number of polymer-anchored ligands containing oxygen atom(s) have been reported⁶, however, there is no report on the coordination compounds of polymer-anchored ligands containing urea moiety. In view of their pronounced coordinating properties, we thought it worthwhile to synthesize and characterize the polystyrene-anchored Schiff base PSCH₂-LH₃ (**1**) and its coordination compounds with Cu(II), Co(II), Zn(II), Cd(II), Mn(II), Ni(II), Fe(III), MoO₂(VI), Zr(OH)₂(IV) and UO₂(VI). It is expected that the present compounds may find use in some of the fields mentioned above.

EXPERIMENTAL

Chloromethylated polystyrene [PSCH₂-Cl] (containing 1.17 mmol of Cl per g and 1 % cross-linked with divinylbenzene

[Sigma Chemical Co. (USA)], manganese(II) acetate tetrahydrate, dioxouranium(VI) acetate dihydrate, iron(III) chloride (anhydrous), (Sarabhai); copper(II) acetate monohydrate (IDPL); cobalt(II) acetate tetrahydrate, cadmium(II) acetate dihydrate, hexadecaquaoctahydroxotetrazirconium(IV) chloride, *o*-aminophenol (BDH); nickel acetate tetrahydrate (Fluka); zinc acetate dihydrate, ammonium molybdate tetrahydrate, methanol, DMF, ethyl acetate, triethylamine (Ranbaxy) were used as supplied for the syntheses. 3-Formylsalicylic acid, bis(acetylacetonato)dioxomolybdenum(VI), hexadecaquaoctahydroxotetrazirconium(IV) acetate and polystyrene 3-formylsalicylate were synthesized by adopting the published procedures⁷.

Synthesis of polystyrene-anchored Schiff base (PSCH₂-LH₃, **1):** Polystyrene 3-formylsalicylate (1.0 g) was swollen in DMF (50 mL) for 45 min. To this suspension, *o*-hydroxyphenylurea (0.711 g, 4.68 mmol) and ethyl acetate (100 mL) were added while stirring magnetically and the mixture was refluxed for 8 h. The solid product obtained was suction filtered, washed with DMF, ethyl acetate, MeOH and dried *in vacuo* at

room temperature. IR bands (KBr): 1515 [$\nu(\text{C}=\text{O})\phi(\text{aldehyde moiety})$], 1528 [$\nu(\text{C}=\text{O})\phi(\text{amino moiety})$], 1630 [$\nu(\text{C}=\text{N})$ (azomethine)], 1725 [$\nu(\text{C}=\text{O})$ (ester)] and 1735 cm^{-1} [$\nu(\text{C}=\text{O})$ (carbonyl)].

General procedure for the syntheses of compounds 2-8 *i.e.*, [$\text{PSCH}_2\text{-LH}_2\text{M}(\text{OAc})(\text{DMF})$] (**2**) (where $\text{M} = \text{Cu}, \text{Co}$), [$\text{PSCH}_2\text{-LH}_2\text{M}'(\text{OAc})(\text{DMF})$] (**3**) (here $\text{M}' = \text{Zn}, \text{Cd}$), [$\text{PSCH}_2\text{-LH}_2\text{M}''(\text{OAc})(\text{DMF})_3$] (**4**) ($\text{M}'' = \text{Mn}, \text{Ni}$), [$\text{PSCH}_2\text{-LH}_2\text{FeCl}_2(\text{DMF})_2$] (**5**), [$\text{PSCH}_2\text{-LH}_2\text{MoO}_2(\text{acac})$] (**6**) ($\text{acacH} = \text{pentane-2,4-dione}$), [$\text{PSCH}_2\text{-LH}_2\text{Zr}(\text{OH})_3(\text{DMF})_2$] (**7**) and [$\text{PSCH}_2\text{-LH}_2\text{UO}_2(\text{OAc})(\text{DMF})$] (**8**): 1.0 g of $\text{PSCH}_2\text{-LH}_3$ (**1**) was allowed to suspend and swell in DMF (100 mL) for 1 h. A DMF solution of appropriate metal salt/compound (2.34 mmol) was added to the above suspension. The mixture was refluxed on a water bath for 8-10 h and the products obtained were suction filtered, washed several times with ethyl acetate and DMF. The products were then dried as mentioned above.

Analyses and physical measurements: The estimation of metal contents/coordinated DMF molecules, spectral studies on the polystyrene-anchored coordination compounds were carried out as reported earlier⁸.

RESULTS AND DISCUSSION

Polystyrene-3-formylsalicylate ($\text{PSCH}_2\text{-3-fsal}$) is obtained by reacting $\text{PSCH}_2\text{-Cl}$ and 3-formylsalicylic acid in 1:4 molar ratio in DMF in the presence of triethylamine. It is worthwhile to note that if the above ratio is kept < 1:4, 100 % conversion does not take place. Polystyrene-3-formylsalicylate reacts with *o*-hydroxyphenylurea in DMF in 1:4 molar ratio and forms the polystyrene-anchored Schiff base, $\text{PSCH}_2\text{-LH}_3$ (**1**). The latter reacts with appropriate metal salt/compound and forms the corresponding polystyrene-anchored coordination compounds. The percent reaction conversion (PRC) of the compounds lies between 44.7-81.3 (Table-1) and the metal binding capacity (MBC) of **1** between 0.32-0.60 mmol of metal per gram of the latter. **1** and its coordination compounds (**2-8**) are insoluble in water and in common organic solvents. DMF has been chosen as the solvent due to its high dielectric constant and more effective in swelling the resin. DMF is lost completely by heating **2-5**, **7** and **8** in air-oven.

3-Formylsalicylic acid exhibits the $\nu(\text{C}=\text{O})$ (carboxylic) stretch⁷ at 1660 cm^{-1} . The appearance of a new band at 1725 cm^{-1} due to the $\nu(\text{C}=\text{O})$ (ester) stretch in $\text{PSCH}_2\text{-3-fsal}$ is indicative of the covalent bond formation *via* ester linkage⁹.

The disappearance of the broad feature of the -OH group on anchoring with $\text{PSCH}_2\text{-Cl}$ also suggests the bond formation between -OH group of carboxylic moiety and $-\text{CH}_2\text{Cl}$ group of chloromethylated polystyrene moiety⁹. The band at 1250 cm^{-1} in $\text{PSCH}_2\text{-Cl}$ due to the $\nu(\text{C}-\text{Cl})$ stretch, disappears in $\text{PSCH}_2\text{-3-fsal}$, which further supports the covalent bond formation¹⁰. The resulting polystyrene-anchored Schiff base (**1**) shows prominent bands at 1735, 1725, 1630, 1528 and 1515 cm^{-1} due to the $\nu(\text{C}=\text{O})$ (carbonyl), $\nu(\text{C}=\text{O})$ (ester), $\nu(\text{C}=\text{N})$ (azomethine), $\nu(\text{C}-\text{O})\phi(\text{amino moiety})$ and $\nu(\text{C}-\text{O})\phi(\text{aldehyde moiety})$ stretches, respectively. The band due to the $\nu(\text{C}-\text{O})\phi$ (aldehyde moiety) undergoes a positive shift by $\leq 10 \text{ cm}^{-1}$ in compounds **2-8** which indicates the involvement of phenolic O atom of the aldehydic moiety⁷ towards coordination. The data rule out the adoption of the bimetallic structure by compounds **2-8**. The $\nu(\text{C}-\text{O})\phi$ (amino moiety) stretch remains almost unaltered in compounds **1** and **2-8** indicating the non-involvement of phenolic O atom of amino moiety towards coordination. The shifting of the $\nu(\text{C}=\text{N})$ (azomethine) stretch towards lower energy by 10-25 cm^{-1} in compounds **2-8** suggests the participation of azomethine N towards coordination⁷. The $\nu(\text{C}=\text{O})$ (ester) stretch remains at the same energy in compounds **2-8** indicating the non-participation of the ester O atom(s) on coordination. The $\nu(\text{C}=\text{O})$ (carbonyl) stretch occurring at 1735 cm^{-1} also remains unaltered in compounds **2-8** ruling out the possible enolisation and coordination of O atom upon coordination. Although compound **1** is potentially a pentadentate ligand, but IR data indicate its bidentate coordination mode through phenolic O and azomethine N atoms. The presence of the new non-ligand bands between 521-550 and 430-470 cm^{-1} due to the $\nu(\text{M}-\text{O})$ and $\nu(\text{M}-\text{N})$ stretches support the coordination through O and N atoms, respectively of compound **1**¹¹. The $\nu_{\text{as}}(\text{OAc})$ and $\nu_{\text{s}}(\text{OAc})$ stretches of free acetate ions occur at 1560 and 1416 cm^{-1} , respectively¹². The appearance of the bands in compounds **2-4** and **8** between 1585-1595 and 1345-1390 cm^{-1} due to the $\nu_{\text{as}}(\text{OAc})$ and $\nu_{\text{s}}(\text{OAc})$ stretches, respectively indicates the presence of the coordinated acetato group in these compounds. The energy separation (204-240 cm^{-1}) between $\nu_{\text{as}}(\text{OAc})$ and $\nu_{\text{s}}(\text{OAc})$ stretches is > 144 cm^{-1} which indicates the monodentate nature of the acetato ligand. DMF shows a band at 1680 cm^{-1} due to the $\nu(\text{C}=\text{O})$ stretch¹³. This band shifts to lower energy by 10-40 cm^{-1} in compounds **2-8** except **6** and this indicates the involvement of O atom of DMF towards

TABLE-1
ANALYTICAL, MBC AND PRC VALUES OF POLYSTYRENE-ANCHORED COORDINATION COMPOUNDS

S. No.	Compound	Observed (calculated) (%)		MBC* (mmol/g of resin)	PRC**
		D	DMF		
1	2 (M=Cu)	2.9 (4.84)	3.3 (5.56)	0.46	59.9
2	2 (M=Co)	3.2 (4.50)	4.0 (5.58)	0.54	71.1
3	3 (M'=Zn)	2.7 (4.98)	3.0 (5.55)	0.41	54.2
4	3 (M'=Cd)	6.4 (8.25)	4.2 (5.36)	0.57	77.5
5	4 (M''=Mn)	2.5 (3.79)	9.9 (15.10)	0.46	66.0
6	4 (M''=Ni)	2.3 (4.04)	8.4 (15.06)	0.39	56.9
7	5	1.8 (4.02)	4.7 (10.50)	0.32	44.7
8	6	5.8 (7.13)	–	0.60	81.3
9	7	3.7 (6.49)	5.9 (10.39)	0.40	57.01
10	8	7.5 (15.67)	2.3 (4.80)	0.32	47.9

*MBC = [M % (observed) \times 10]/(atomic weight of metal). **PRC = [M % (observed) \times 100]/M % (calculated) on the basis of 100 % reaction conversion of polystyrene-anchored ligand to polystyrene-anchored coordination compounds.

TABLE-2
 IR, REFLECTANCE SPECTRAL DATA (cm⁻¹) AND MAGNETIC MOMENTS OF THE COORDINATION COMPOUNDS

S.N.	Compound	$\nu(\text{C}=\text{N})$ (azomethine)	$\nu(\text{C}-\text{O})(\phi)$	$\nu_{\text{as}}(\text{OAc})$	$\nu_{\text{s}}(\text{OAc})$	$\nu(\text{C}=\text{O})$ (DMF)	ν_{max}	Magn. moment (BM)
1	1	1630	1515	–	–	–	–	–
2	2 (M=Cu)	1618	1522	1587	1362	1656	18,700	1.87
3	2 (M=Co)	1610	1518	1585	1345	1655	8650, 25000	2.55
4	3 (M'=Zn)	1608	1517	1594	1390	1670	–	Diamagnetic
5	3 (M'=Cd)	1620	1523	1595	1355	1662	–	Diamagnetic
6	4 (M''=Mn)	1615	1520	1594	1358	1653	18500, 22870, 25700	5.84
7	4 (M''=Ni)	1612	1519	1590	1366	1640	9150, 15780, 25720	3.32
8	5	1605	1523	–	–	1668	12250, 15800, 22200	5.82
9	6	1615	1518	–	–	–	–	Diamagnetic
10	7	1611	1524	–	–	1644	–	Diamagnetic
11	8	1617	1523	1588	1376	1658	–	Diamagnetic

coordination¹³. The presence of bands at 935 and 905 cm⁻¹ in compound **6** due to the $\nu_{\text{s}}(\text{O}=\text{Mo}=\text{O})$ and $\nu_{\text{as}}(\text{O}=\text{Mo}=\text{O})$ stretches, respectively suggest the presence of a *cis*-MoO₂ configuration in it¹⁴. Acetylacetonone is coordinated in compound **6** as a monobasic bidentate OO donor ligand as evident by the presence of a band at 1695 cm⁻¹ due to the $\nu(\text{C}=\text{O})$ stretch¹⁵. The absence of a band between 950-850 cm⁻¹ characteristic of the $\nu(\text{Zr}=\text{O})$ stretch¹⁶ and the appearance of a band at 1125 cm⁻¹ due to the $\delta(\text{Zr}-\text{OH})$ bending mode support the formulation of compound **7** as [PSCH₂-LH₂Zr(OH)₃(DMF)₂] and not as [PSCH₂-LH₂ZrO(OH)₂(H₂O)(DMF)₂]¹⁴. The appearance of band at 895 cm⁻¹ in compound **8** due to the $\nu_{\text{as}}(\text{O}=\text{U}=\text{O})$ stretch suggests the presence of a *trans*-UO₂(VI) configuration in it¹⁴.

The reflectance spectrum of compound **2** (M=Cu) shows a broad band at 18700 cm⁻¹ due to the ²B_{1g} → ²A_{1g}, ²B_{2g} and ²E_g transitions for the square-planar arrangement of compound **1** around Cu(II) ion¹⁷. The existence of bands at 8650 and 25000 cm⁻¹ corresponding to the ¹A_{1g} → ¹B_{2g} and ¹A_{1g} → ¹B_{1g} transitions, respectively indicates the square-planar geometry¹⁸ around Co(II) ion in compound **2** (M=Co). Compound **4** (M''=Ni) shows three bands at 9150, 15780 and 25720 cm⁻¹, due to the ³A_{2g}(F) → ³T_{2g}(F)(v₁), ³A_{2g}(F) → ³T_{1g}(P)(v₂) and ³A_{2g}(F) → ³T_{1g}(F)(v₃) transitions, respectively in an octahedral environment¹⁷. The v₂:v₁ value is 1.7, which lies in the usual range (1.6-1.82) for octahedral Ni(II) complexes. The spectral parameters are: Dq = 915 cm⁻¹, B = 886.12, β = 0.86, % covalance = 14.0 and LFSE = -131.45 kJ mol⁻¹. The reduction of Racah parameter from the free ion value of 1030 to 886.12 cm⁻¹ and the percentage covalance value (14.0) indicate the covalent nature of the compound and strong field nature of compound **1**¹⁹. Compound **4** (M''=Mn) exhibits three bands at 18500, 22870 and 25700 cm⁻¹ due to the ⁶A_{1g} → ⁴T_{1g}(G)(v₁), ⁶A_{1g} → ⁴T_{2g}(G)(v₂) and ⁶A_{1g} → ⁴A_{1g}(G)(v₃) transitions, respectively in the compound¹⁷. Compound **5** shows three bands at 12250, 15800 and 22200 cm⁻¹ due to the ⁶A_{1g} → ⁴T_{1g}(G)(v₁), ⁶A_{1g} → ⁴T_{2g}(G)(v₂) and ⁶A_{1g} → ⁴A_{1g}(G)(v₃) transitions in octahedral symmetry¹⁷. It is of interest to note that although both Mn(II) and Fe(III) have ⁶A_{1g} ground state, all bands occur in compound **5** at lower energy than those of compound **4** (M''=Mn). This is due to the lower value of Racah parameter (B and C) in compound **5** to those of compound **4** (M''=Mn)¹⁷.

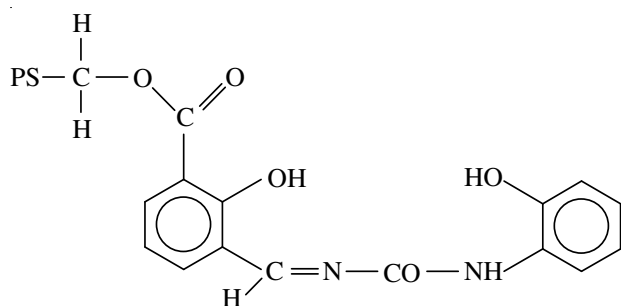
The room temperature magnetic susceptibilities and magnetic moments of compounds **2**, **4** and **5** are presented in the Table-2. The magnetic moment of compound **2** (M=Cu) is

1.87 BM which is in the expected range reported for magnetically dilute Cu(II) compounds²⁰. Compound **2** (M=Co) shows a magnetic moment of 2.55 BM which corresponds to the square-planar geometry around the metal ion²¹. The magnetic moment of compound **4** (M''=Ni) is 3.32 BM indicating octahedral geometry around the Ni(II) ion²¹. Compound **4** (M''=Mn) displays a magnetic moment of 5.84 BM which is expected for high-spin, magnetically dilute Mn(II) compound²¹. The magnetic moment of compound **5** is 5.82 BM which is closer to spin-only value indicating an octahedral complex²¹.

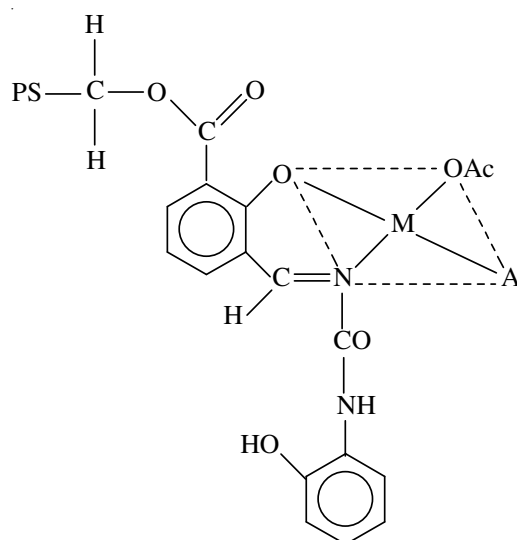
The X-band ESR spectrum of compound **2** (M=Cu) has been recorded in DMSO at 77 K using DPPH as marker. The spectrum shows usual anisotropic pattern with two g values, which are characteristic of axial symmetry. The spin-Hamiltonian parameters of the complex are: A_{||} = 1.70 × 10⁻² cm⁻¹, A_⊥ = 3.2 × 10⁻³ cm⁻¹, g_{||} = 2.24, g_⊥ = 2.08, g_{av} = 2.1, G = 3.15, P_d = 1.76 × 10⁻² cm⁻¹, κ = 0.48, g_{||}/A_{||} = 132, α² = 0.79. The pattern g_{||} > g_⊥ > 2 suggests a tetragonal distortion around Cu(II) ion corresponding to elongation along four-fold symmetry z axis with d_{x²-y²} as the ground state²². The value of g_{||} is less than 2.3 suggesting the covalent character of compound **2** (M=Cu). The value of G (3.15) is less than 4, which is indicative of strong field nature of compounds **1** in **2** (M=Cu)²³. The value of covalent parameter, α² (in-plane σ bonding) is 0.79 which suggests the considerable covalent bonding²³. The lower value of P_d in comparison to the free ion value (3.5 × 10⁻²) indicates the presence of covalent character between metal-ligand bonding. The absence of a band at ca. 1500 gauss due to the ΔM_s = 2 transition in the present case precludes the presence of Cu-Cu interaction. This results a magnetically dilute environment around the metal atom as the pathway for dimer formation is blocked.

Conclusion

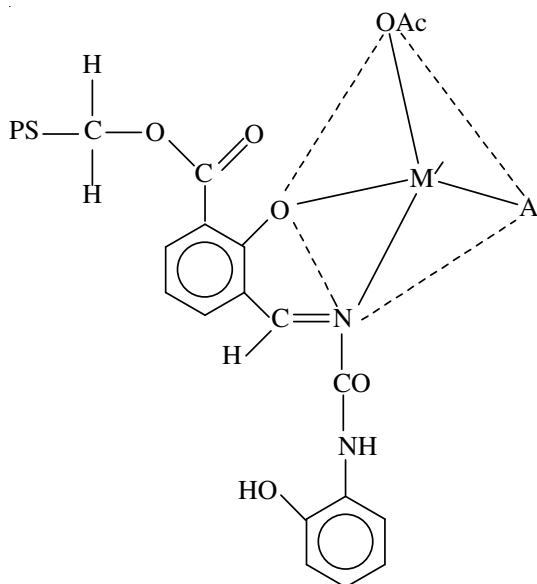
The polystyrene anchored Schiff base, PSCH₂-3fsalohypru **1** is capable of acting as chelating ligand. It behaves as a monobasic bidentate ON donor ligand and coordinates with a variety of metal ions to form 1:1 metal-ligand compounds. The ligand and its coordination compounds with Cu(II), Co(II), Zn(II), Cd(II), Mn(II), Ni(II), Fe(III), MoO₂(VI), Zr(OH)₂(IV) and UO₂(VI) ions have been synthesized and characterized by elemental analyses, spectral studies and magnetic susceptibilities measurements and the suggested structures of present complexes are given below:



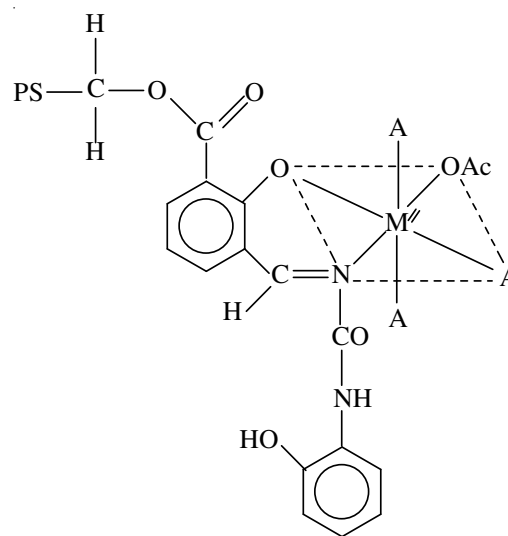
[1]



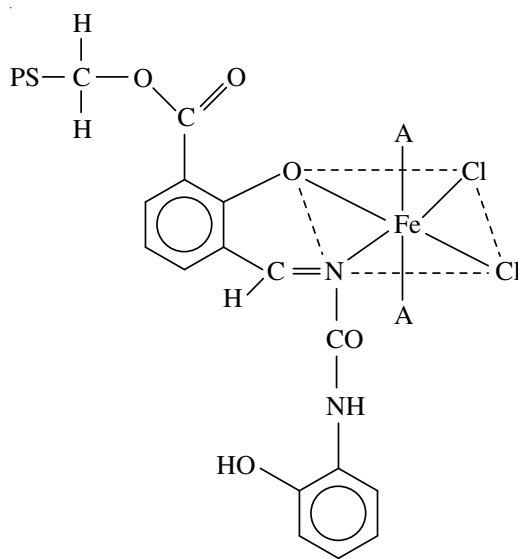
[2; M = Cu, Co]



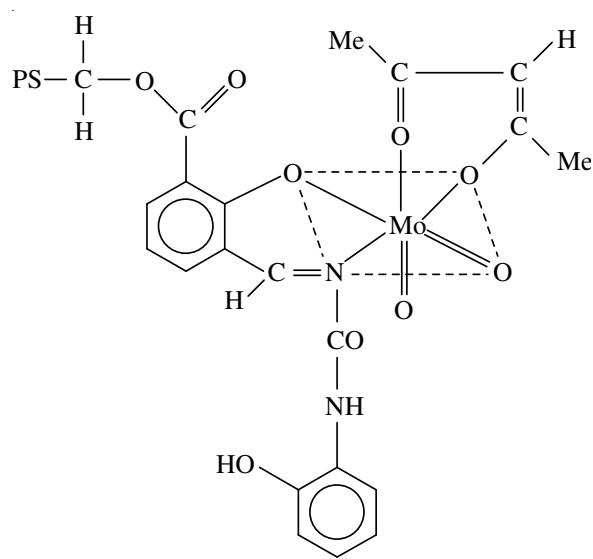
[3; M' = Zn, Cd]



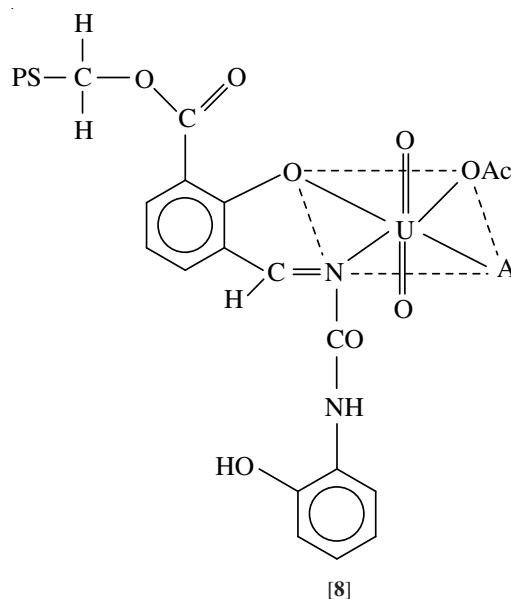
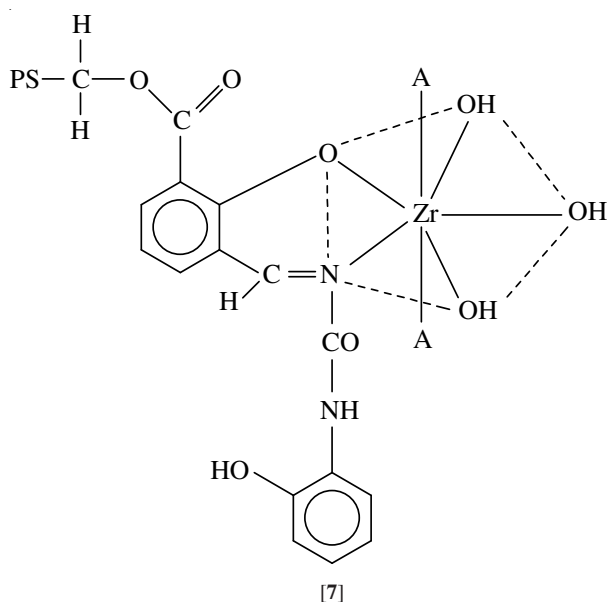
[4; M'' = Mn, Ni]



[5]



[6]



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