

Synthesis and Characterization of 4-methoxyaniline Dithiocarbamate Complexes with Iron (II), Cobalt (II), Nickel (II), Cadmium (II), Silver (I)

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ABSTRACT

New complexes of dithiocarbamate of the general formula $[M M' (4 - \text{MeoAndtc})_4]$, $[M [M' (4 - \text{MeoAndtc})_2]_2]$, $[M (1, 10 \text{ phen})_3]$, $[M' (4 - \text{MeoAndtc})_4]$ and $[M (1, 10 \text{ phen})_3]$, $[M' (4 - \text{MeoAndtc})_6]$ where $M = \text{Fe(II), Co(II), Ni(II)}$, $M' = \text{Cd(II) and Ag(I)}$. (4-MeoAndtc) = 4-Methoxyaniline dithiocarbamate. (1, 10 phen) = 1, 10 phenanthroline. Have been prepared and characterized by atomic absorption spectroscopy, infrared, conductance measurements, electronic spectra, and magnetic susceptibility measurements. Magnetic moment and electronic spectra indicate that the complexes of the type $[M M' (4 - \text{MeoAndtc})_4]$ and $[M [M' (4 - \text{MeoAndtc})_2]_2]$ are of square planar geometry while the complexes of the type $[M (1, 10 \text{ phen})_3]$, $[M' (4 - \text{MeoAndtc})_4]$ and $[M (1, 10 \text{ phen})_3]$, $[M' (4 - \text{MeoAndtc})_6]$ have octahedral geometry.

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INTRODUCTION

Dithiocarbamates are valuable compounds due to their interesting chemistry and wide utilities and application one of the most interesting aspects of dithiocarbamates is their applications in coordination chemistry (Azim *et al.*, 2011).

Most of aliphatic and aromatic dithiocarbamate synthesized until now may coordinate only through the dithio-group behaving as uninegative bidentate ligands in reactions with metal ions (Leka *et al.*, 2006).

Dithiocarbamate complexes continue to attract attention due to their ability to stabilize transition metals in a variety of oxidation states and a developing interest in this area is the functionalisation of the dithiocarbamate substituent (Graeme *et al.*, 2009).

Transition metal dithiocarbamate complexes find use in diverse applications such as material science medicine and agriculture. (Shaheen *et al.*, 2007), and possess interesting structural chemistry (Onwudiwe and Ajibade, 2011), that make their study continuously attractive and biological activity (as antibacterial, cytostatic, antifungal and immunoregulatory) most of these applications are based on complexation properties of dithiocarbamate ligands with metal ions especially with transition metal ions (Golcu, 2006).

In view of these interesting results we have prepared a new dithiocarbamate ligand and its complexes with different metal ions and their nitrogenous adducts.

EXPERIMENTAL

Materials and Methods:

All chemicals used in the present work were of analytical reagent (A. R.) grade (B. D. H. or Fluka) infrared spectra were recorded on Brucker 27 Alpha A. T. R.-diamond, Lazer spectrophotometer in the $400\text{--}4000\text{ cm}^{-1}$ range without using KBr discs. Conductivity measurements were carried out on a 10^{-3} M solution of the complexes in DMF using conductivity meter Jenway 4510 at ambient temperature. The electronic spectra were recorded on ashimadzu. UV-visible spectrophotometer UV-(650 Pc for 10^{-3} M solution of complexes in DMF as solvent at 25°C using 1 cm quartz cells. Metal content were determined using 3000 atomic absorption. Melting points were recorded on an electrothermal 9100 apparatus.

The magnetic measurement was carried out at 19°C on the solids by Sherwood scientific instrument.

Synthesis of Sodium 4-Methoxyaniline Dithiocarbamate:

Aqueous solution of (4.0 gm, 0.1 mol) of sodium hydroxide was added to ethanoic solution of (12.3 gm, 0.1 mol) of 4-methoxyaniline. With stirring. The mixture was cooled in an ice bath. To this mixture (7.6 cm^3 , 0.1 mol) of carbon disulfide was added drop wise with continuous stirring for 30 min in ice bath. The precipitate formed was extracted with (100 ml) diethyl ether. Filtered off washed with diethyl ether and dried under vacuum, a white precipitate formed.

1- A synthesis of complex $[M(M' - 4 - \text{MeoAndtc})_4]$ $M = \text{Fe(II)}, \text{Co(II)}, \text{Ni(II)}, M' = \text{Cd(II)}$:

Aqueous solution of (0.308 g, 0.001 mol) of $[\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}]$ was added drop wise with continuous stirring to aqueous solution of (0.884 gm, 0.004 mol) of the ligand to form $\text{Na}_2[\text{Cd}(4\text{-MeoAndtc})_4]$, 80: 20 % Acetone-water solution of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (0.278 gm, 0.001 mol) or $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.291 gm, 0.001 mol) or $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.291 gm, 0.001mol) was added drop wise with continuous stirring for 30 min until complete precipitation, the precipitate was filtered off, washed with ethanol then with diethyl ether and dried under vacuum.

1- B synthesis of complex $[M[M'(4 - \text{MeoAndtc})_2]_2]$ $M = \text{Fe(II)}, \text{Co(II)}, \text{Ni(II)}, M' = \text{Ag(I)}$:

Aqueous solution of AgNO_3 (0.34 gm, 0.002 mol) was added drop wise with continuous stirring to aqueous solution of ligand (0.884 gm, 0.004 mol) to form $\text{Na}_2[\text{Ag}(4\text{-MeoAndtc})_2]_2$ compound and similarly as in I-A metal salts of Fe(II) , Co(II) and Ni(II) was added drop wise with continuous stirring for 30 min. The precipitate formed was filtered and washed with ethanol then dried under vacuum.

1-C synthesis of complex $[M(1, 10 \text{ phen})_3][M'(4 - \text{MeoAndtc})_4]$ $M = \text{Co(II)}, \text{Ni(II)}, M' = \text{Cd(II)}$:

Prepared by adding mixture of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.29 gm, 0.001mol) or $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.29 gm, 0.001 mol) and 1, 10 phenoathnoline (0.54 gm, 0.003mol) dissolved in 80: 20% acetone-water to $\text{Na}_2[\text{Cd}(4\text{-MeoAndtc})_4]$ (0.9505 gm, 0.001mol) which prepared in 1-A with continuous stirring for 30 min. The mixture was leaved for 3-days to complete the reaction. The precipitate formed was filtered, washed with acetone then dried under vacuum.

1-D synthesis of complex $[M(1, 10 \text{ phen})_3][M'_2(4 - \text{MeoAndtc})_6]$ $M = \text{Co(II)}, \text{Ni(II)}, M' = \text{Cd(II)}$:

Prepared by adding a mixture of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.29gm, 0.001mol) or $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.29gm, 0.001 mol) and (1, 10 phen) (0.54gm, 0.003 mol) dissolved in 80 : 20% acetone water to $\text{Na}_2[\text{Cd}_2(4\text{-MeoAndtc})_6]$ which prepared by adding $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (0.617gm, 0.002 mol) to the ligand (1.326 gm . 0.006 mol) drop wise with continuous stirring for 30 min. the precipitate formed was filtered'-washed with ethanol then dried under vacuum.

RESULTS AND DISCUSSION

The new ligand was prepared by the reaction of 4-Methoxyaniline with sodium hydroxide and then added Carbon-disulphide. The complexes were prepared through direct reaction of the metal nitrate $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ or AgNO_3 with $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ or $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ or $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ with the above ligand. The values of conductivity in dimethyl formamide solution of the complexes range from (8.22-16.9) $\text{cm}^2 \cdot \text{Ohm}^{-1} \cdot \text{mol}^{-1}$ for the complex $[M M'(4 - \text{MeoAndtc})_4]$ and $[M[M'(4 - \text{MeoAndtc})_2]_2]$ which are typical values for non-electrolyte type

(Geary, 1971) while the values of conductivity of the complexes of the type $[M(1,10\text{ phen})_3]$ $[M'(4 - \text{MeoAndtc})_4]$ and $[M(1,10\text{ phen})_3][M'_2(4 - \text{MeoAndtc})_6]$ range from $(72.2-84.1)\text{cm}^2\text{ Ohm}^{-1}\text{ mol}^{-1}$ which are typical values for electrolyte type (C. Preti and G. Tosi, 1974).

Infrared Spectral Studies:

The important IR bands of the ligand and its complexes are listed in Table (2). The stretching frequency of the $\nu(\text{C}\cdots\text{N})$ band for the dithiocarbamate was intermediate between the stretching frequencies associated with typical single and double-bonded carbon and nitrogen atoms (Srinivasan *et al.*, 2010).

The $\nu(\text{C}\cdots\text{N})$ and $\nu(\text{C}\cdots\text{S})$ of complex type $[MM'(4 - \text{MeoAndtc})_4]$ and $[M[M'(4 - \text{MeoAndtc})_2]_2]$ were observed in the range of $(1608-1636)\text{cm}^{-1}$ and $(968-988)\text{cm}^{-1}$. The presence of only one band in the later region reports the bidentate coordination of the dithioligand (Serano, 2003). IR spectra of complex type $[MM'(4 - \text{MeoAndtc})_4]$ and $[M[M'(4 - \text{MeoAndtc})_2]_2]$ showed a new band at $(433-493)$ which are evidence for the coordination of metal to sulfur $\nu(\text{M} - \text{S})$. This behaviour may be attributed to the electron releasing of the amines which forces high electron density towards the sulfur atoms. Also the $\nu(\text{M}' - \text{S})$ was observed in the range $(401-460)\text{cm}^{-1}$ for the same complexes. The IR spectra of complexes of type $[M(1,10\text{ phen})_3]$ $[M'(4 - \text{MeoAndtc})_4]$ and $[M(1,10\text{ phen})_3][M'_2(4 - \text{MeoAndtc})_6]$ showed one band at $(419-450)\text{cm}^{-1}$ which are evidence for the coordination of metal to sulfur $\nu(\text{M}' - \text{S})$ in addition to the $\nu(\text{M}-\text{N})$ was observed in the range $(478-513)\text{cm}^{-1}$ region (Raya *et al.*, 2006) in the adduct.

Electronic Spectral Studies:

The UV visible spectra of the ligand and its complexes of 10^{-3}M solution in DMF were recorded the results were listed in table (2). The UV-visible spectrum of the Fe(II) complex (1) gives absorption bands at $(10225)\text{cm}^{-1}$, $(12019)\text{cm}^{-1}$ and $(39063)\text{cm}^{-1}$ regions, the UV-visible of Fe(II) complex (4) gives absorption bands at $(32258)\text{cm}^{-1}$ and $(41666)\text{cm}^{-1}$ regions which corresponds to (d-d) transition in square planar geometry (Nicholls, 1973).

The Co(II) complex (2) exhibited an absorption band at $(15772)\text{cm}^{-1}$ region which was assigned $(^2A_{1g} \rightarrow ^2E'g)$ transition and the Co(II) complex (5) exhibited an absorption band at $(25641)\text{cm}^{-1}$ region which was assigned to

$(^2A_{1g} \rightarrow ^2E'g)$ transition (Bailar *et al.*, 1973).

The Ni(II) complex (3) show two absorption bands at $(22936)\text{cm}^{-1}$ and $(25126)\text{cm}^{-1}$ which were assigned to $(^1A_{1g} \rightarrow ^1A_{2g})$ and $(^1A_{1g} \rightarrow ^1B_{1g})$ transitions in square planar geometry.

The Ni(II) complex (6) show two absorption bands at $(22727)\text{cm}^{-1}$ and $(25126)\text{cm}^{-1}$ which were assigned to $(^1A_{1g} \rightarrow ^1A_{2g})$ and $(^1A_{1g} \rightarrow ^1B_{1g})$ transitions in square planar geometry (Pandeya *et al.*, 1981).

The complexes (7 and 9) show two absorption bands in the regions $(17483)\text{cm}^{-1}$, $(25000)\text{cm}^{-1}$ for complex (7) and $(10460)\text{cm}^{-1}$, $(29440)\text{cm}^{-1}$ for complex (9) which were assigned to $(^4T_{1g}(\text{F}) \rightarrow ^4A_{1g}(\text{F}))$ and $(^4T_{1g}(\text{F}) \rightarrow ^4T_{1g}(\text{P}))$ transition in an octahedral geometry of high spin (Martell, 1971).

The complexes (8 and 10) show three absorption bands in the region $(10571)\text{cm}^{-1}$, $(28409)\text{cm}^{-1}$ $(45045)\text{cm}^{-1}$ for complex (8) and in the region $(13298)\text{cm}^{-1}$, $(31056)\text{cm}^{-1}$, $(44248)\text{cm}^{-1}$ which were assigned to $(^3A_{2g}(\text{F}) \rightarrow ^3T_{2g}(\text{F}))$, $(^3A_{2g}(\text{F}) \rightarrow ^3T_{1g}(\text{F}))$, $(^3A_{2g}(\text{F}) \rightarrow ^3T_{1g}(\text{P}))$ transition in octahedral configuration (Singh *et al.*, 1989).

Magnetic susceptibility measurements:

The magnetic moments of the complexes table (1) were measured at 19°C . The magnetic moments for Fe(II), Co(II) and Ni(II) complexes (1 to 6) were $(1.80 - 3.84\text{ B.M})$ suggesting a square planar geometry (Larkworthy *et al.*, 1968). The low value of magnetic moment for complex (5) is due to ant ferromagnetic interaction.

The magnetic moments of other complexes (7 to 10) were in the range $(2.74 - 4.60\text{ B.M})$ in an octahedral geometry (Nicholls, 1973)

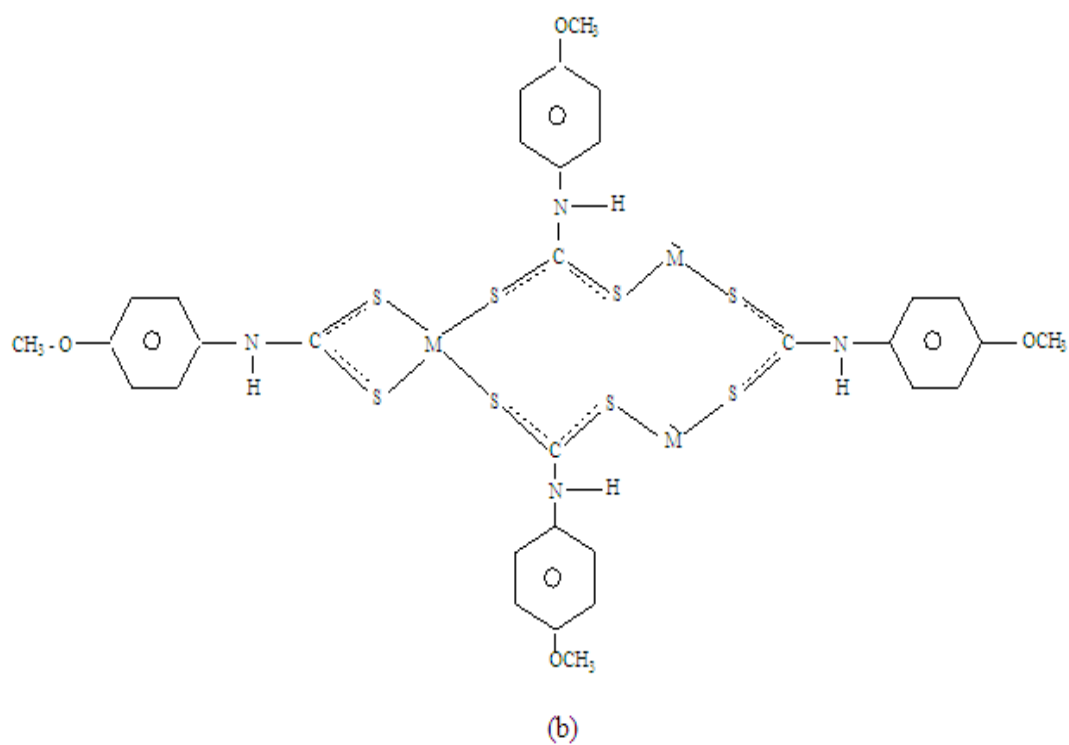
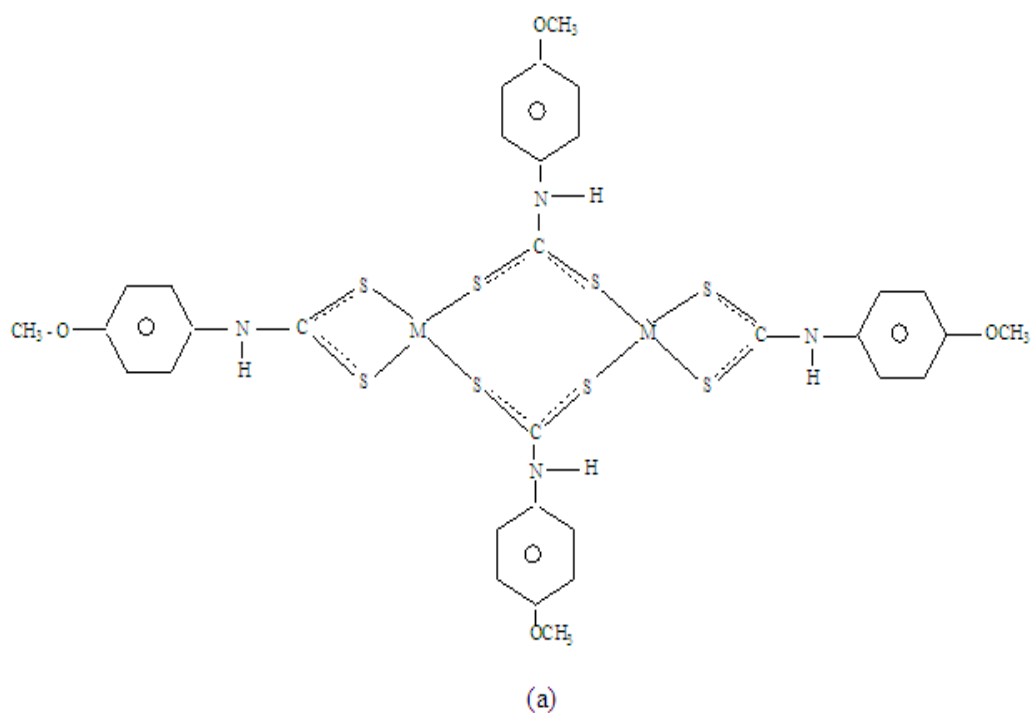
Table (1): Analytical and some physical properties of the prepared complexes

No.	Compound	Color	m.p° C	Molar conductivity	% M	%yield	μ eff B.M
L	C ₈ H ₈ NOS ₂ Na	White	142				
1	[FeCd(4-MeoAndtc) ₄]	Orange	270	10.16	5.42 (5.81)	53	3.50
2	[CoCd(4-MeoAndtc) ₄]	Dark green	260	16.9	5.75 (6.12)	55	3.08
3	[NiCd(4-MeoAndtc) ₄]	Green yellow	180	12.8	5.69 (6.09)	81	diamagnetic
4	[Fe{Ag(4-MeoAndtc) ₂ } ₂]	Dark brown	250	8.22	4.85 (5.25)	69	3.84
5	[Co{Ag(4-MeoAndtc) ₂ } ₂]	Black	190	9.28	5.12 (5.53)	71	1.80
6	[Ni{Ag(4-MeoAndtc) ₂ } ₂]	Dark brown	194	15.19	5.15 (5.50)	64	diamagnetic
7	[Co(1, 10phen ₃)[Cd(4-MeoAndtc) ₄]	Brown	180	72.2	3.64 (3.92)	67	4.58
8	[Ni(1, 10phen ₃)[Cd(4-MeoAndtc) ₄]	Light yellow	230	76.6	3.58 (3.90)	70	2.74
9	[Co(1, 10phen ₃)[Cd ₂ (4-MeoAndtc) ₆]	Brown	170	80.5	2.76 (2.93)	64	4.60
10	[Ni(1, 10phen ₃)[Cd ₂ (4-MeoAndtc) ₆]	Light yellow	170	84.1	2.67 (2.91)	66	3.18

Table (2): IR bands (cm⁻¹) and electronic spectra of ligand and prepared complexes.

No.	Compound	U.V bands cm ⁻¹	IR spectra (cm ⁻¹)				
			$\nu(\text{C} \cdots \text{N})$	$\nu(\text{C} \cdots \text{S})$	$\nu(\text{M} - \text{S})$	$\nu(\text{M}' - \text{S})$	$\nu(\text{M} - \text{N})$
L	C ₈ H ₈ NOS ₂ Na		1507	490	
1	[FeCd(4-MeoAndtc) ₄]	10225 12019 39063	1614	988	479	401	...
2	[CoCd(4-MeoAndtc) ₄]	15772	1613	987	433	413	...
3	[NiCd(4-MeoAndtc) ₄]	22936 25126	1508	988	472	460	...
4	[Fe{Ag(4-MeoAndtc) ₂ } ₂]	32258 41666	1636	968	478	424	...
5	[Co{Ag(4-MeoAndtc) ₂ } ₂]	25641	1608	968	493	449	...
6	[Ni{Ag(4-MeoAndtc) ₂ } ₂]	22727 25126	1613	970	472	460	...
7	[Co(1, 10phen ₃)[Cd(4-MeoAndtc) ₄]	17483 25000	1456	1030	...	441	513

8	[Ni(1, 10phen ₃)[Cd(4-MeoAndtc) ₄]	10571 28400 45045	1456	1029	...	419	478
9	[Co(1, 10phen ₃)[Cd ₂ (4-MeoAndtc) ₆]	10460 29940	1460	1030	...	450	511
10	[Ni(1, 10phen ₃)[Cd ₂ (4-MeoAndtc) ₆]	13298 31056 44248	1467	1030	...	441	510



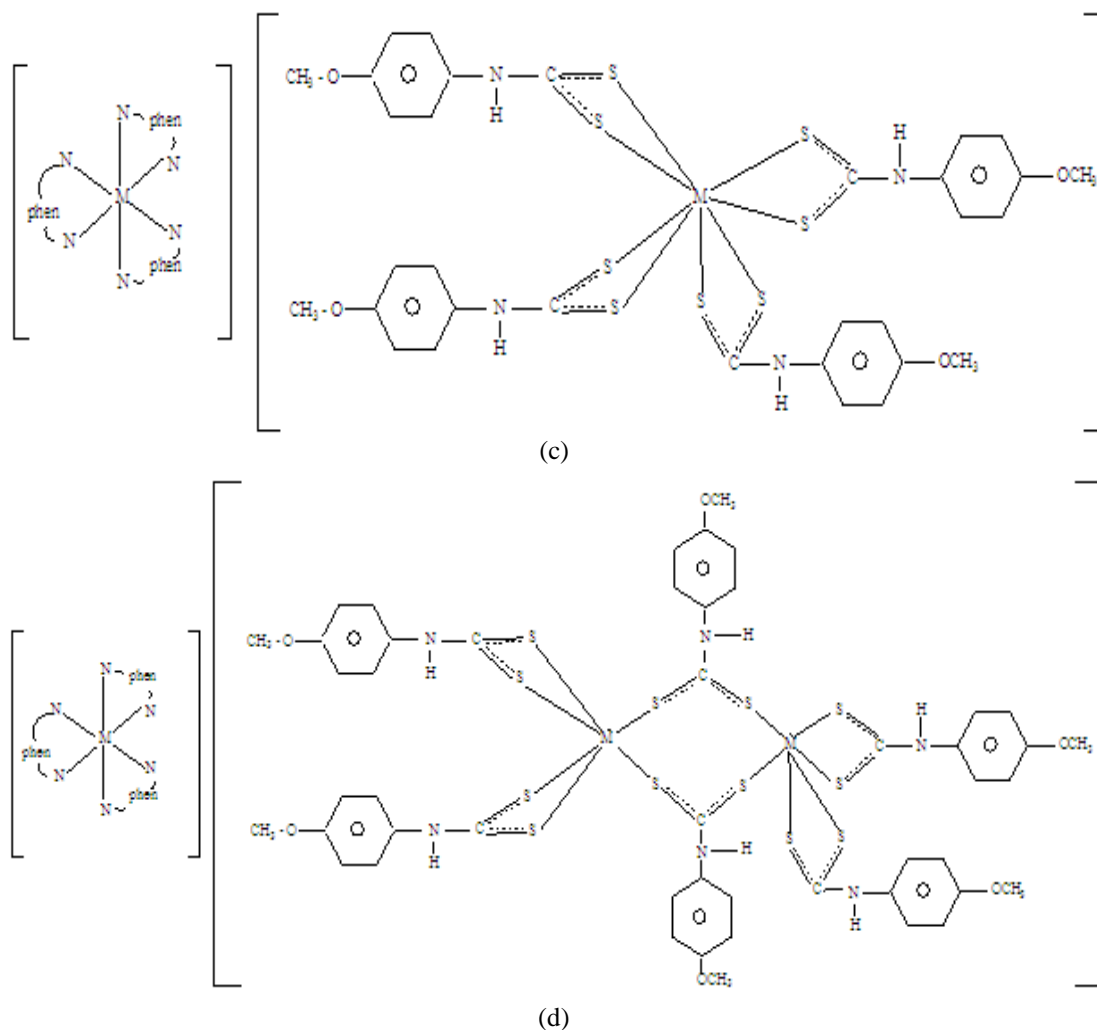


Fig: suggest structures (a): complexes [1, 2, 3], (b): complexes [4, 5, 6], (c): complexes [7, 8], (d): complexes [9, 10]

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