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SYNTHESIS AND CHARACTERIZATION OF TRANSITION METAL COMPLEXES OF DITHIOCARBAMATE DERIVATIVE OF DIPHENYLAMINE

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ABSTRACT

The transition metal complexes of the type ML_2 [Where L=dithiocarbamate derivative of Diphenylamine and M=chlorides of [Cr(III),Mn(II),Fe(III), Co(II),Ni(II),Cu(II) and Cd(II)] were synthesized by the reaction of metal chloride with ligand L in the 1:2 molar ratio. The resulting complexes have been characterized on the basis of elemental analysis, IR spectral analysis, conductivity measurement, antimicrobial activities. Analysis of results reviles that the complexes shows square planer, tetrahedral and octahedral geometry, non-electrolytic nature and having more antimicrobial activity than the ligands. The ligands are bonded to metal through two sulphur atoms and acting as bidentet ligand.

KEYWORDS: Dithiocarbamate, Diphenylamine, transition metals.

INTRODUCTION

Dithiocarbamate complexes of transition metals are known to have large scale biological effects with various applications as antifungals, herbicides and insecticides among many other medical applications.[1] Dithiocarbamates (DTCs) are the synthetic compounds which are involved in the formation of complexes with most of the stable transition metals in a various oxidation states. DTCs draw Much attention is drawn by dithiocarbamate complexes in recent years and a large number of DTCs complexes have been synthesized on a large scale in the last 50 years.[2-5] A new synthetic strategy has been reported to prepare the DTCs.[5] Dithiocarbamate derivative contain azo group. There fore Azo compounds are an interesting materials that have shown a range of applications including; food technology, analytical chemistry, pharmaceutical application and dyeing or textile industry. Their role in coloring approach has been widely investigated and a range of compounds are fabricated.[6] The biological activity of azo-compounds allowed them to be used in the treatment of textile materials, also azo-compounds are well known for their medicinal importance and have shown a variety of applications as antitumor, antibacterial, antiseptics and antineoplastics.[7] Variety of ligands type Schiff-base and their metal complexes have been isolated, these compounds have very flexible and diverse structures, therefore their properties have been studied.[8] Dithiocarbamates (DTCs) are class of organic compounds that are capable to chelate to metal ions.[9,10] DTCs compounds have a significant role in coordination chemistry. This may due to the metal ion stabilization tendency in many oxidation states, and permitting the metal ion to implement its desirable structure[11] DTCs have shown a significant biological activity including their role as antibacterial, antitumor and antifungal agents. The fungicidal activity of dithiocarbamate of alkali, alkaline earth and transition metals has been known for a long time[14-22] and these complexes showed selective activities towards some of the test microorganisms. Transition metal dithiocarbamate complexes are known to have large scale biological effects with various applications as herbicides and insecticides among many other medical applications.[23] They are also being studied for their use in agrochemicals, pharmaceuticals, intermediates in organic synthesis, as protecting group in peptide synthesis or as chelators in materials chemistry. Dithiocarbamate ligands have extensive coordination chemistry and wide range of applications.[24-28]

MATERIALS AND METHODS

The compounds metal chlorides, sodium hydroxide, carbon disulphide and diphenylamine used were of analytical grade. The amount of metals are determined volumetrically by using EDTA complexometrically using indicator Eriochrome Black T for Cr(III) and Mn(II), Varamine blue for Fe(III), Xylenol orange for Co(II) and Cd(II), while mureoxide is used for Ni(II) and Cu(II).Cu(II) is estimated idometrically using starch as an indicator. IR spectra of the complexes were recorded on JASCO 6700 make FTIR spectrophotometer in the region 400-4000 cm^{-1}, electronic spectra were recorded on JASCO 670 UV-Visible spectrophotometer in the range 200-1400 nm from our DST funded Instrumentation Laboratory. Antimicrobial activities were determined by using three anti microbial nutrients from department of Microbiology Pratap College, Amalner.

Synthesis of Ligand: Dithiocarbamate derivative of Diphenylamine

Take 2 gram Diphenylamine dissolved into 15-20 ml distilled water cool at 0°C in water bath. Take 3ml of CS_2 solution and cool at 0°C in water bath. If the solution is turbid, add Alcohol or water until a clear solution is obtained .Heat the mixture on Micro oven for 3 to 4 minutes. Shake well and allow to stand for 10 minutes. The compound crystallizes from the cold solution on standing. Therefore cool the reaction mixture ice water. Filter the crystal on Buchner funnel; wash the precipitate with cold water. The solid product was recrystallized from hot ethanol and record the melting point.

Reaction

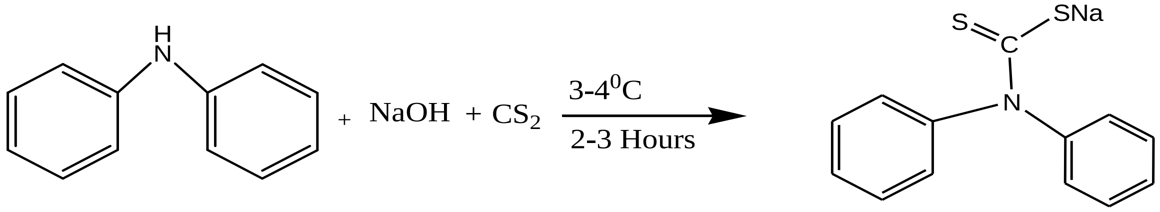


Table 1: The physical properties of ligands.

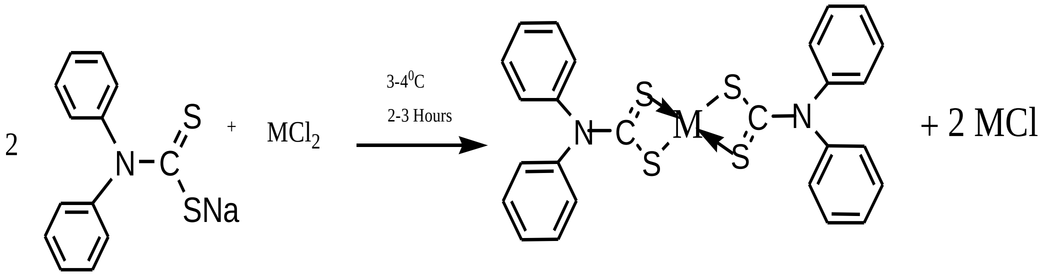
Ligand	Mol. Formula	Mol. wt	Melting point	Method of purification
Dithiocarbmate derivative Dipaminenylamine	$C_{13}H_{10}Ns2Na$	169	52°C	Ethyl alcohol

SYNTHESIS OF METAL COMPLEXES

In the synthesis of all the transition metal complexes, the following general procedure was used.

To 20ml of 0.01M alcoholic solution of metal chloride and 20 ml of 0.02M alcoholic solution of dithiocarbmate derivative of diphenylamine was added with continuous stirring at room temp in an ice bath. Then the solution was cooled to ice temperature for 1-2 hours. The colored solid complex separates out from solution. The solid product is filtered, washed with methanol, dried and weight of the complex obtained is taken to determine practical yield.

Reaction



RESULTS AND DISCUSSION

The complexes formed were having different colors which are insoluble in chloroform, carbon tetrachloride, methanol, ethanol but soluble in DMF. The physical properties of complexes were indicated in table 2. The TLC of complexes ML_2 and ligand L was taken. It exhibit single spot with R_f values being different from the ligand.

The amount of metals present in complexes were determined complex metrically by EDTA using Erichrome black T, xylenol orange, varamine blue as an indicator. Specific conductance were measured at room temperature in DMF by a Systronics direct reading 304 conductivity meter using a glass conductivity cell having a cell constant one. Antimicrobial activities were determined in the PG department of Microbiology, Pratap College, Amalner by using three microbial nutrients. The elemental analysis indicates that, all the metal complexes have 1:2 stoichiometry and are, soluble only in DMF and DMSO. The molar conductance values obtained for these complexes at the concentration of 10^{-3} M are in the range of 3-13 ohm^{-1} mol^{-1} cm^{2} indicating non electrolytic nature of complexes.

Sr. No.	**Complex**	**Colour**	**Mol wt**	**% of Metal** (Calcu.).	**% of C**	**% of N**	**% of S**	**% of H**
1	Ligand	Yellow	386	-	55.95	7.25	36.16	3.62
2	Cd(dithiocarbamate derivative of diphenylamine)$_2$	White	498.41	(22.55) 22.41	43.33	5.61	25.68	2.80
3	Co(dithiocarbamate derivative of diphenylamine)$_2$	Dirty White	444.93	(13.24) 13.27	48.54	6.35	29.02	3.19
4	Cr(dithiocarbamate derivative of diphenylamine)$_2$	White	437.94	(11.86) 11.81	49.32	6.39	29.22	3.19
5	Cu(dithiocarbamate derivative of diphenylamine)$_2$	Black	449.54	(14.13) 14.19	48.04	6.22	28.44	3.11
6	Fe(dithiocarbamate derivative of diphenylamine)$_2$	Shiny Green	441.85	(12.64) 12.71	48.88	6.33	28.96	3.16
7	Mn(dithiocarbamate derivative of diphenylamine)$_2$	White	440.93	(12.45) 12.67	48.98	6.35	29.02	3.19
8	Ni(dithiocarbamate derivative of diphenylamine)$_2$	Faint Green	444.69	(13.19) 13.25	48.57	6.29	28.78	3.14

IR Spectra of complexes

IR spectra were recorded in the region of 4000-400 cm^{-1} on JASCO 6700 FTIR Spectrophotometer. Three important bands are expected in the IR spectra of dithiocarbamate compounds. The first one is the band in the range 1541-1515 cm^{-1} corresponding to ν(C-N) stretching vibrations.[29] The second one is the vibration in the finger print region in the range 1189–1168 cm^{-1}, associated with ν(C-S) bands.[30] The third important band occurs at far infrared region and is associated with the ν(M-S) vibration in the range 416-414 cm^{-1}.[31] The infrared spectra of the ligands and their corresponding complexes were compared and carefully assigned. In the ligand, the ν(N-H) which is due to the N-H bond of the amine was observed at 3159cm^{-1} and there was no shift of this peak in the complex, this indicates that the N-H was not bonded to the metal ion. In the spectra of the ligands, two bands were observed for the υ(C-S) symmetrical and asymmetrical stretching vibrations and these appeared as a single sharp bands in the spectra of all the complexes. This indicates that the dithiocarbamate ligands are bonded to the metal ions as bidentate chelating ligands.[32] In case of chromium and iron complexes two bands are observed one in the range 406-403 cm^{-1} due to ν(M-Cl) indicating presence of M-Cl bond in the structure and second in the range 3445-4-3435 cm^{-1} ν(-OH) of water molecule, indicating participation water molecule in the structure.

Sr. No.	Ligand/complex	V_{NH}	$V_{-OH(H20]}$	V_{C-S}	V_{C-N}	V_{M-S}	V_{M-Cl}
1	Ligand	3159	-	1189	1541		
2	[Cd(dithiocarbamate derivative of diphenylamine)$_2$]	3159		1171	1527	414	
3	[Co(dithiocarbamate derivative of diphenylamine)$_2$]	3159	-	1177	1523	416	
4	[Cr(dithiocarbamate derivative of diphenylamine)$_2$(H$_2$O)Cl]	3159	3635	1175	1515	416	403
5	[Cu(dithiocarbamate derivative of diphenylamine)$_2$]	3158		1170	1521	413	
6	[Fe(dithiocarbamate derivative of diphenylamine)$_2$(H$_2$O)Cl]	3159	3645	1169	1524	417	406
7	[Mn(dithiocarbamate derivative of diphenylamine)$_2$]	3159		1173	1527	414	
8	[Ni(dithiocarbamate derivative of diphenylamine)$_2$]	3159		1168	1523	414	

Electrical conductivity of the complexes

All the complexes are insoluble in water, ethanol, benzene and soluble in DMF. The electrical conductivity of the solutions is measured by using Equiptronics conductivity meter with inbuilt magnetic stirrer model (Eq-664) at room temperature. Molar conductivity data shows that only chromium (III)and Fe(III) complexes shows electrolytic nature of complexes while all other complexes are non-electrolytic in nature.

Sr. No.	**complex**	**Molar conductivity**
1	[Cd(dithiocarbamate derivative of diphenylamine)$_2$]	1.0
2	[Co(dithiocarbamate derivative of diphenylamine)$_2$]	1..1
3	[Cr(dithiocarbamate derivative of diphenylamine)$_2$(H_2O)Cl]	24.0
4	[Cu(dithiocarbamate derivative of diphenylamine)$_2$]	1.4
5	[Fe(dithiocarbamate derivative of diphenylamine)$_2$(H_2O)Cl]	24.2
6	[Mn(dithiocarbamate derivative of diphenylamine)$_2$]	0.87
7	[Ni(dithiocarbamate derivative of diphenylamine)$_2$]	0.97

Microbiological Activities

The macro cyclic ligand and macro cyclic ligand complexes synthesized in the present investigation has been subjected to antimicrobial screening programs based on their structural features so as to ascertain their activity against four different microorganisms *E.coli., Baciullus Sp Staphylococcus sp., and Pseudomonas.*

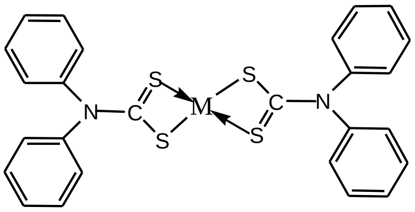
The solvent used was DMSO, and the sample concentrations were, 100ppm. The results of preliminary study on antimicrobial activity indicated that most of the complexes show activity as shown against these organisms.

Table 5: Microbiological activities (zone inhibition in mm).

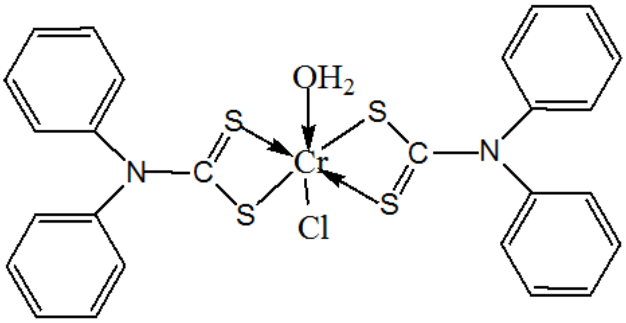
Name of ligand/complex	**E.coli**	**Bacillus**	**Staph**	**Pseudomonas**
Ligand	13	14	-	-
[Cd(dithiocarbamate derivative of diphenylamine)$_2$]	12	-	-	12
[Co(dithiocarbamate derivative of diphenylamine)$_2$]	10	10	-	17
[Cr(dithiocarbamate derivative of diphenylamine)$_2$(H_2O)Cl]	-	-	-	13
[Cu(dithiocarbamate derivative of diphenylamine)$_2$]	-	-	12	12
[Fe(dithiocarbamate derivative of diphenylamine)$_2$(H_2O)Cl]	-	-	13	19
[Mn(dithiocarbamate derivative of diphenylamine)$_2$]	12	10	-	-
[Ni(dithiocarbamate derivative of diphenylamine)$_2$]	-	10	19	23

By considering all the above properties of the dithiocarbamate complexes, the complexes of Mn(II),Co(II),Ni(II),Cu(II) and Cd(II) were formulated as four coordinate species in which the metal ions are coordinated to two molecules of dithiocarbamate ligands through the sulfur atoms acting as bidentate chelating ligands, while the complexes of Cr(III) and Fe(III) were formulated as six coordinate species in which the metal ions are coordinated to two molecules of dithiocarbamate ligands through the sulfur atoms acting as bidentate chelating ligands and other two coordinating species are one water molecule and one chlorine atom., the structure of complexes are as shown below.

Structure of Dithiocarbmate Complex of Mn(II),Co(II),Ni(II),Cu(II) AND Cd(II)



Structure of Dithiocarbmate Complex of Cr(III) and Fe(III)



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