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Thermoanalytical and Antimicrobial Studies of *o*-Amino-N,N-dipropylbenzylamine Complexes With Cobalt(II), Nickel(II) and Iron(II)

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o-Amino-N,N-dipropylbenzylamine complexes with Co(II), Ni(II) and Fe(II) are reported. Evaluation of the nature of complexes has been carried out on the basis of spectroscopic and analytical techniques. Thermal behaviour of the complexes has been studied by the thermogravimetric and differential thermal analysis. Antimicrobial activity of *o*-amino-N,N-dipropylbenzylamine and its metal complexes are reported against some pathogenic bacteria and fungi by diffusion plate method.

Key Words: Synthesis, *o*-Amino-N,N-dipropylbenzylamine, TGA, DTA, Antimicrobial activity.

INTRODUCTION

Transition metal complexes are the class of chemical substances, which have attracted great interest for their applications in industrial and synthetic processes such as catalysis, materials synthesis, photochemistry and biological systems. Their synthesis and theoretical study by the long period of time has resulted in the introduction of new aspects of analysis[1].

There are few reports available in the literature regarding the reaction of N,N-dialkylbenzylamine and their derivatives with metals in relatively common and stable oxidation states. So as to get an idea about the utility of these amines and their derivatives as chelating organic reagents for the analysis of metals especially having functional groups such as -OH, -SH, -COOH, -NH_2 *etc*., preparative routes and stabilities of the complexes with metals need to be explored[2].

N,N-Dialkylbenzylamine and its derivatives containing -OH, -NH_2 *etc*., groups can act as effective chelating agents. The compounds are capable of forming six membered ring systems which would enhance the stabilities of the complexes formed with metals in favourable oxidation states[3]. By knowing the stability of these complexes, it has become increasingly possible to synthesize new chelating agents and their use in analytical chemistry[4]. Recent studies on the chemistry of chelate forming molecules containing donor atoms like nitrogen, oxygen, *etc*. has been quite revealing[5].

Interest in orthometalated complexes arises from their potential application in organic synthesis[6], in catalysis[7,8] as chiral resolving agents[9,10] as drugs[11] and as new materials[12]. Orthopalladation using lithium tetrachloropalladate(II) was observed with N,N-dimethylbenzylamine or some of its aryl substituted derivatives containing electron releasing group[13,14].

Bhatia *et al.*[15] have synthesized a number of organo mercury complexes such as RHgCl·L (R = Ph, L = isoniazid) and characterized thermogravimetrically and thermodynamic parameters for thermal degradation. Dash *et al.*[16] worked on the thermal studies of complexes of cobalt(II) and nickel(II) with N-methylimidazol. Thermoanalytical studies of benzylidenaniline and phenylazophenyl complexes with I B and II B metals have also been reported[17,18].

Complexes of *o*-nitro-N,N-dimethylbenzylamine with Cu(II), Ag(I), Au(III), Zn(II), Cd(II) and Hg(II) have been synthesized and were also investigated for their antimicrobial activities against some pathogenic bacteria and fungi[19,20]. The derivatives of *o*-nitro-N,N-diethylbenzylamine with Fe(II), Ni(II) and Co(II) have been synthesized and their thermal behaviour and relative stabilities were also studied by thermogravimetric and differential thermal analysis[21]. The present work is related to N,N-dialkylbenzylamine derivative. N,N-Dialkylbenzylamines are capable of co-ordination to metals through nitrogen.

EXPERIMENTAL

N-Bromosuccinimide, carbon tetrachloride, benzoyl peroxide, sodium bicarbonate, *o*-toluidine, ferrous sulphate, nickel chloride and cobalt chloride were purchased from E. Merk with certified purity of 99 %. Dipropylamine was obtained from Fluka. All chemicals were used without further purification. Solvents were purified in accordance with standard methods.

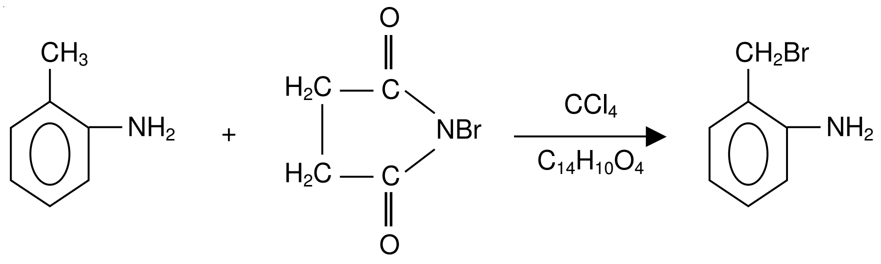
Melting/decomption points of the complexes were taken on Gallenkamp melting point device model No.1002 and are uncorrected. Viscocity of ligand was determined by using techino VS 250 viscometer size No. B.S/IP/RF. Water was used as a reference solvent. The surfacetension of the ligand was determined by stalagmometer and refractive index was taken on Abbe's refractometer.

Infrared spectra of the ligand and complexes were recorded in thin film and KBr disc, respectively, in the spectral range of 4000-400 cm^{-1} on Hitachi infrared spectrophotometer, Model 270-30. λ_{max} of ligand was taken in CCl_4 on Hitachi UV visible spectrophotometer, Model U-2000. Estimation of metal was carried out on Hitachi atomic absorption spectrophotometer, Model Z-8000, chlorine by Stepnow method and nitrogen was estimated by Kjeldahl's method. C, H and S of complexes was done by using Carlo Erba Elenmental analyzer, Model EA-1108.

Thermogravimetric and differential thermal analysis (TG/DTA) was carried out in air on a NETZSCH simultaneous thermal analyzer, Model STA-409 in the temperature range of 0-1200 °C. Calcined alumina was used as reference material. Experimental weight losses within different temperature ranges were calculated and correlated to the theoretical weight losses of expected decomposition products. The residue left after igniting the complexes were analyzed by atomic absorption spectroscopy and XRD.

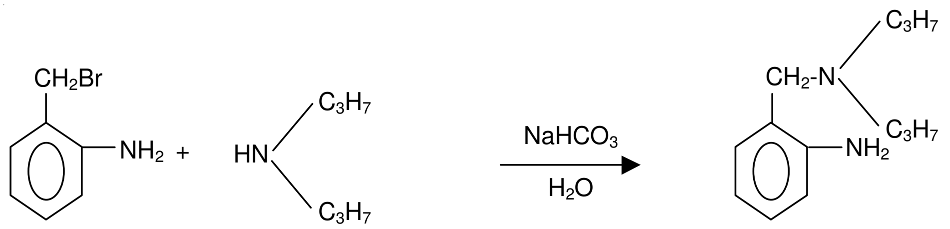
Synthesis of *o*-amino-N,N-dipropylbenzylamine

Bromination of *o*-toluidene: Bromination was carried out by method of Farooq *et al.*[22] as outlined below. *o*-Toluidene (0.5 mol), N-bromosuccinimide (0.5 mol) and benzoyl peroxide (1.0 g) in CCl_4 (250 mL) were charged in a quickfit flask equipped with water condenser and reaction mixture was heated under reflux for 6-8 h, until all the solid started floating on the liquid surface. The mixture was allowed to cool down to room temperature and regenerated succinimide was filtered off. The filtrate was evaporated to give *o*-amino benzylbromide.



o-Toluidine N-Bromo succinimide *o*-Amino benzylbromide

Synthesis: *o*-Amino benzylbromide, sodium bicarbonate (0.5 mol) and distilled water (100 mL) were taken in a quickfit flask (500 mL) equipped with water condenser. Dipropylamine (0.5 mol) was added and mixture was again refluxed for 4 h. The mixture was transferred to a separating funnel where two layers were formed. The organic layer was collected and passed through a column packed with silica gel No. 60 (70-230 mesh size). The *n*-hexane:ether (3:1) eluted a brown fraction which on evaporation gave light brown thick oily liquid (compound-**I**), soluble in almost all organic solvents. It was used without further purification (yield 60.1 %).



o-Amino benzylbromide Dipropylamine *o*-Amino-N,N-dipropylbenzylamine

(Compound **I**)

Reaction of *o*-amino-N,N-dipropylbenzylamine with cobalt(II) chloride and nickel(II) chloride: *o*-Amino-N,N-dipropylbenzylamine (6.0 m mol) dissolved in ethanol was added to cobalt(II) chloride and nickel(II) chloride (3.0 m mol) in distilled water followed by the addition of 3-4 drops of liquid NH_3. The reaction mixture was heated in water bath till ammonia ceased to evolve. Purple and light green solid settled which was filtered and washed with distilled water, ethanol and *n*-hexane and dried to get compound (**II**) and (**III**) as purple and light green solid, decomposition point > 300 °C.

Reaction of *o*-amino-N,N-dipropylbenzylamine with ferrous(II) sulphate: *o*-Amino-N,N-dipropylbenzylamine (6.0 m mol) was dissolved in ethanol. Clear solution of ferrous(II) sulphate (3.0 m mol) was prepared in distilled water by warming. Both the solutions were mixed and stirred for 3-4 h. A brown solid settled which was filtered and washed with warm distilled water, ethanol and *n*-hexane and dried to get compound (**IV**) as brown solid decomposition point > 300 °C.

Antimicrobial activity: Antimicrobial activity of ligand and their metal complexes was investigated by agar diffusion method[23] against *Pseudomona aeruginosas*, *Bacillus subtilis*, *Escherichia coli*, *Staphylococcus aureus*, *Aspergillus niger*, *Rhizopus nigrificans* and *Penicillium citrovenim*. Assay medium was adjusted before the addition of agar. The nutrient agar was also used for the bioassay. The bioassay medium consisted of (g/L) beef extract 1, yeast extract 2, peptone 5, NaCl 5, agar 15 and water 1000 mL. pH of the medium was adjusted before the addition of agar. The medium was then dispensed in 250 mL Erlenmeyer flask and sterilized at 121 °C and 15 ψ pressure for 15 min.

Preparation of petri plates: The petri plates were washed and sterilized in oven at 120 °C overnight. 20 mL of the molten bioassay medium poured in the sterile plates was allowed to set. 4 mL of molten assay medium was incubated with predetermined concentrations of the microorganisms and spread uniformly over the first layer and was allowed to set. Then four wells of 0.8 cm were made in the plates aseptically using stainless steel borer. An emulsion of sample in gumacacia was used for testing its antimicrobial activity. 0.12 mL of the emulsion was added to a hole incubated at 37 °C for 24 h. Clear zones of inhibition were developed and the diameter of the zones of inhibition was measured in mm.

RESULTS AND DISCUSSION

The light brown oily ligand obtained by the prescribed method was having relative density of 0.955 g/mL at 26 °C, boiling point 198 °C, λ_{max} 298.5 nm, refractive index 1.623 at 26 °C, viscosity 28.56 g/cm/s at 26 °C and surface tension 29.25 dynes/cm at 26 °C.

The infrared spectra are given in Table-1. IR spectra of *o*-amino-N,N-dipropylbenzylamine and its metal complexes show N-H stretching vibrations in the range 3400-3172 cm^{-1}. The absorption bands indicated around 3100-3028 cm^{-1} are assigned to Ar-H vibration. N-H bending vibration was depicted in the 1625-1510 cm^{-1} region of the spectra. C-N of the type Ar-NH_2 was observed in the range 1380-1220 cm^{-1}. The absorption bands at 1360-957 cm^{-1} may be assigned to in-plane bending of ring C-H and bands near 840-660 cm^{-1} are due to out of plane bending. IR spectra of complexes show lowering of frequency in the 1623-1240 cm^{-1} region of the spectra which indicates co-ordinate bond formation. Some new bands below

TABLE-1
INFRARED SPECTRA OF COMPOUNDS

Compounds	Infrared absorption bands (ν) cm^{-1}
I	3888 (s), 3316 (m), 3172 (w), 3100 (w), 3064 (m), 3028 (w), 1623 (s), 1605 (m), 1596 (m), 1461 (s), 1380 (m), 1344 (m), 1326 (m), 1254 (w), 1191 (m), 1155 (w), 1065 (m), 1038 (w), 957 (w), 813 (m), 777 (s), 732 (m), 687 (w)
II	3450 (w), 3400 (w), 3340 (w), 3060 (w), 2995 (w), 2875 (w), 1600 (m), 1555 (w), 1510 (w), 1480 (w), 1460 (w), 1360 (w), 1220 (w), 1160 (w), 1110 (w), 1040 (w), 1020 (w), 840 (m), 700 (s), 660 (w), 585 (w), 505 (w), 440 (w), 419 (w)
III	3406 (m), 3384 (w), 3300 (w), 3100 (w), 3028 (w), 3010 (w), 2974 (w), 2920 (w), 2884 (w), 1623 (w), 1605 (w), 1506 (w), 1461 (w), 1434 (w), 1380 (w), 1362 (w), 1245 (w), 1146 (w), 1065 (w), 1020 (w), 975 (w), 885 (w), 786 (w), 687 (w), 525 (w), 480 (w), 435 (w), 417 (w), 408 (w)
IV	3400 (m), 3320 (w), 3190 (w), 3080 (w), 2895 (w), 1600 (m), 1590 (w), 1520 (w), 1460 (w), 1370 (w), 1240 (w), 1140 (w), 1030 (w), 875 (w), 750 (w), 660 (w), 585 (m), 520 (w), 430 (w), 410 (w)

600 cm^{-1} may be assigned to M-N bonds. The lowering in position of bands also depicts the formation of metal complexes[24]. Elemental analysis and atomic absorption data (Table-2) indicates the formation of metal complexes in the ratio of M:L = 1:1.

TABLE 2
ANALYTICAL DATA OF COMPLEXES

Complexes	Elemental analysis (%): Found (Calcd.)					
	M	N	Cl	C	H	S
II	15.80 (17.54)	7.70 (8.34)	19.15 (21.14)	44.76 (46.44)	4.86 (6.55)	–
III	15.20 (17.46)	7.00 (8.34)	19.86 (21.16)	45.21 (46.48)	5.48 (6.56)	–
IV	13.60 (14.96)	6.80 (7.11)	–	37.52 (39.61)	4.89 (6.60)	6.78 (8.12)

Antimicrobial activity of ligand and its metal complexes was investigated against some pathogenic bacteria and fungi such as *Escherichia coli*, *Pseudomonas aeruginosa*, *Bacillus subtilis*, *Staphylococcus aureus*, *Aspergillus niger*, *Rhizopus nigrificans* and *Penicillium citrovenim* by agar diffusion plate method. The antimicrobial activity of the ligand and its metal complexes were compared with one another and with streptomycin, which was used as a positive control. An emulsion of 5 % gumacacia was used as a negative control, which shows no antimicrobial activity. Ligand shows least activity so data is given in Table-3. The antimicrobial activity of the metal complexes is in the following order;

Ni(II) Complex > Co(II) Complex > Fe(II) Complex.

Thermogravimetric studies have shown that complex of *o*-amino-N,N-dipropylbenzylamine dichlorocobalt (II) is stable up to 260 °C as no weight loss was indicated (Table-4, Fig. 1). The complex is decomposed in the temperature range of 290-370 °C to evolve chlorine (theor. 21.1 %, exp. 19.0 %) followed by an

TABLE-3
ANTIMICROBIAL ACTIVITY OF *o*-AMINO-N,N-DIPROPYLBENZYLAMINE AND IT'S COMPLEXES

Compounds	Concentrations	Diameter of the inhibition zone (mm)						
		E. coli	*P. aeruginosa*	*B. subtilis*	*S. aureus*	*A. niger*	*R. nigrificans*	*P. citrovenim*
$C_{13}H_{22}N_2$	0.12 mL	9.0	10.0	10.0	9.0	10.0	9.0	–
$(C_{13}H_{22}N_2)CoCl_2$	10 mg/mL	–	–	9.0	10.0	9.0	8.0	–
	25 mg/mL	11.0	11.0	12.0	13.0	11.0	10.0	8.0
	50 mg/mL	14.0	16.0	15.0	17.0	14.0	12.0	11.0
$(C_{13}H_{22}N_2)\ NiCl_2$	10 mg/mL	–	9.0	10.0	–	9.0	9.0	–
	25 mg/mL	12.0	15.0	14.0	10.0	14.0	1.20	11.0
	50 mg/mL	18.0	19.0	16.0	17.0	16.0	14.0	12.0
$(C_{13}H_{26}N_2O_2)FeSO_4$	10 mg/mL	–	–	9.0	–	8.0	–	–
	25 mg/mL	11.0	10.0	9.0	9.0	10.0	8.0	–
	50 mg/mL	12.0	11.0	10.0	12.0	11.0	9.0	8.0
Streptomycin	10 mg/mL	17.0	16.0	18.0	15.0	–	–	–
Control	0.12 mL	–	–	–	–	–	–	–

TABLE-4
THERMOGRAVIMETRIC AND DIFFERENTIAL THERMAL ANALYSIS (TGA/DTA)

Compound No.	Temperature range (°C)	Weight loss exp. % (Theor.)	Decomposition product	Exo/endo at (°C)
II	290-370	19.0 (21.1)	Cl_2	320 exo
	400-620	60.0 (61.3)	$C_{13}H_{22}N_2$	450 endo
Residue	1200		CoO	
III	200-280	20.0 (21.1)	Cl_2	260 exo
	400-590	59.0 (61.3)	$C_{13}H_{22}N_2$	530 endo
Residue	1200		NiO	
IV	101	8.0 (9.1)	$2H_2O$	85 endo
	550-650	51.0 (52.3)	$C_{13}H_{22}N_2$	600 endo
	700-730	23.0 (24.3)	$SO_2 + O_2$	700 endo
Residue	1200		FeO	

exothermic peak at 320 °C. Second TG loss was noted from 400-620 °C due to loss of *o*-amino-N,N-dipropylbenzylamine (theor. 61.3 %; exp. 60.0 %) which correspond to an endotherm at 450 °C. The residue corresponding to cobalt oxide confirmed through analysis by atomic absorption and XRD techniques.

o-Amino-N,N-dipropylbenzylamine dichloronickel(II) is stable up to 190 °C (Table-4, Fig. 2). First TG loss was observed in the temperature range of 200-280 °C due to evolution of chlorine (theor. 21.1 %, exp. 20.0 %) followed by an exothermic peak at 260 °C. Second TG loss was noted from 400-590 °C due to loss of *o*-amino-N,N-dipropylbenzylamine (theor. 61.3 %; exp. 59.0 %). DTA showed an endotherm at 530 °C. The residue corresponding to nickel oxide was confirmed through analysis by AAS and XRD.

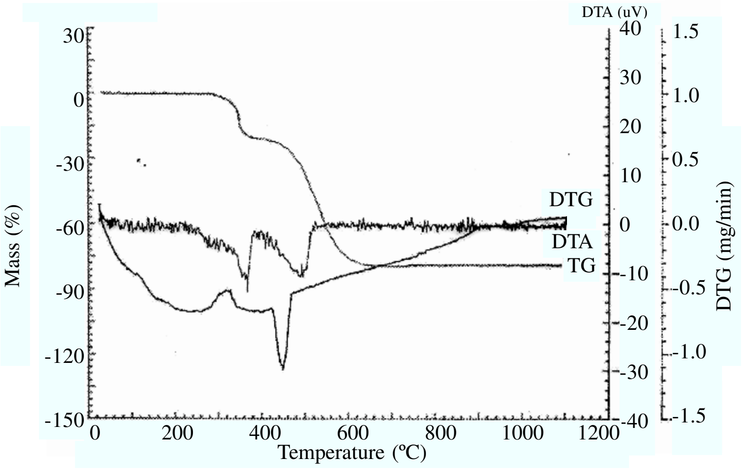


Fig. 1

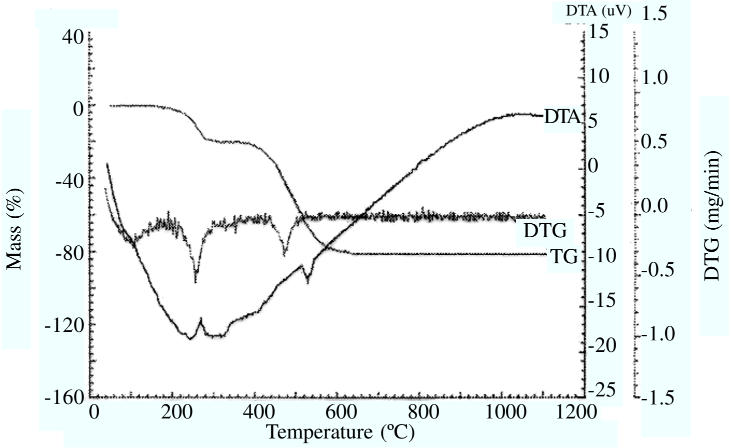


Fig. 2

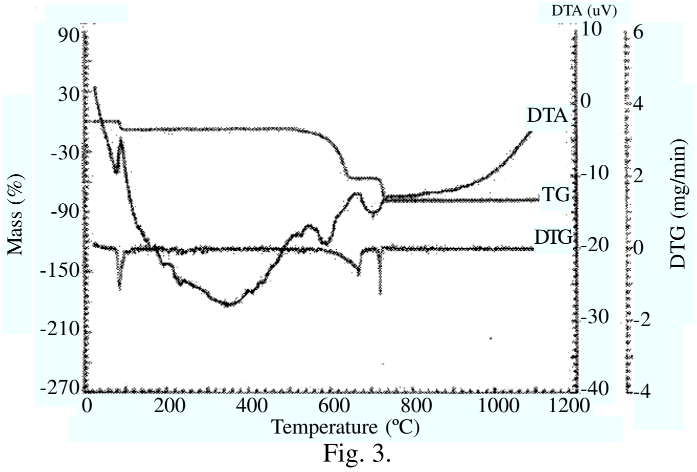


Fig. 3.

In complex of *o*-amino-N,N-dipropylbenzylamine ferrous (II) sulphate, loss of water occurs up to 101 °C with an endotherm at 85 °C (theor. 9.1 %; exp. 8.0 %). The anhydrous complex was stable up to 540 °C and then decomposed to lose *o*-amino-N,N-dipropylbenzylamine (theor. 52.3 %; exp. 51.0 %) at 550-650 °C with an endotherm at 600 °C. Third TG loss was noted from 700-730 °C due to libration of SO_2 and O_2 (theor. 24.3 %, exp. 23.0 %) corresponding to an endothermic DTA peak at 700 °C. The residue corresponding to iron oxide confirmed through analysis by atomic absorption and XRD techniques (Table-4, Fig. 3).

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