Synthetic and Spectroscopic Studies of *m*-Bromo *N, N*-Dimethylbenzylamine and its Complexes with Zn (II) and Cd (II)

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Summary: *m*-Bromo *N,N*-dimethylbenzylamine and its complexes with Zn (II) and Cd (II) metals were synthesized. The nature of *m*-Bromo *N,N*-dimethylbenzylamine and its complexes was evaluated on the basis of UV/ visible and Fourier transformed infrared spectroscopy and analytical data. Estimation of metal contents in the complexes was carried out by atomic absorption spectroscopy. The crystal structure of the complexes was determined by X-ray diffraction spectroscopy.

Introduction

Amines, like ammonia, are weak bases because the unshared electron pair of nitrogen atom can form a coordinate bond with a proton. Aromatic amines are much weaker bases than the aliphatics.

Amines take part in many kinds of chemical reactions and offer many applications which include agrochemicals, dyestuffs (the best known being aniline) pharmaceuticals, and corrosion inhibitors [1]

m-Bromo *N,N*-Dimethylbenzylamine serves as a chelating agent because it occupies more than one coordination sites in the complexes with metals [2]. It is a bidentate ligand because it contains two atoms which can simultaneously donate electron pair, a nitrogen atom and a Br atom [3].

O-cyano-*N, N*-dipropylbenzylamine and its complexes with iron (II), nickel (II) and cobalt (II) have been reported. Evaluation of complexes was carried out on the basis of infrared spectra and analytical data. Antibacterial activity of *o*-cyano-N, N-dipropylbenzylamine and its metal complexes have been reported against some pathogenic bacteria by diffusion plate method [4].

O-Amino N-ethyl-N-phenylbenzylamine and its complexes with zinc (II), cadmium (II) and mercury (II) have been reported. Characterization of the complexes was made on the basis of spectroscopic techniques and analytical data. Compounds have been investigated for their antibacterial activities against *Bacillus subtilis* (B.s.), *Escherichia coli* (E.c.), *Micrococcus luteus* (M.l.) and *Stapylococcus aureus* (S.a.) [5]

Complexes of uranium(VI) and thorium(IV) with *o*-hydroxy *N, N'*-dimethylbenzylamine and *o*-carboxy *N,N'*-dimethylbenzylamine have been synthesized and characterized by elemental analysis, IR and ^{1}H-NMR techniques. The coordination of metal ions with the ligand and their structures have been established. The chemical and spectral properties revealed that uranium(VI) complexes have square bipyramidal structure for coordination number 6, and hexagonal bipyramidal structure for coordination number 8, whereas thorium(IV) shows bicapped square antiprism structure for coordination number 10 [6].

The *o*-carboxy *N-N'*-dimethylbenzylamine uranium(VI) and thorium(IV) complexes, o-$C_6H_4COOHCH_2N$-$(CH_3)_2UO_2SO_4$ (I), o-$C_6H_1COOHCH_2N(CH_3)_2UO_2(NO_3)_2$ (II), o-$C_6H_4COOHCH_2N(CH_3)_2UO_2Cl_2$ (III), and o-C_6H_4CO-$OHCH_2N(CH_3)_2Th(NO_3)_4$ (IV) have been prepared and studied by means of thermoanalytical techniques in static air atmosphere to understand their mode of decomposition and thermal stability. Their compositions have been investigated by elemental analysis in order to ensure their purity, and structure elucidations have based on proton NMR and IR spectroscopy [7].

The Complexes of benzylamine, *N, N*-dimethylbenzylamine and their nitro derivatives have been synthesized with Group IIB and IVA metals. Their proposed formulas have based upon their analytical data, chemical characterization and spectroscopic evidence. [8]

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The Complex $[C_6H_5\text{-}CH_2\ NH\ Me_2]_4[Mo_8O_{26}].4H_2O$ has been synthesized from MoO_3 and $C_6H_5\ CH_2\ NMe_2$, and crystallized. By diffusion, single crystal X-ray analysis, it has been indicated that the crystal belongs to triclinic system, space group P_1, crystal cell parameter a =1.0685(2) nm, b =1.4050(3) nm, c = 1.643(2) nm, $\alpha = 93.12$ (3), $\beta = 110.26(3)$, $\gamma = 71.41(3)$, $\nu = 1.4179$ (5) nm^3, R = 0.0383 [9].

Cyclometalated derivatives of ring substituted N, N-dimethylbenzylamine have been reported with controlled redox potentials as potent mediators of bio-electrochemical electron transport. The cyclo ruthenation of $(C_6H_2R^1Ri^2R^3)CH_2NMe_2(R^1,R^2,R^3= NMe_2)$ with $(\eta^6\text{-}C_6H_5)$ RuCl $(\mu\text{-Cil})_2$ in the presence of $NaOH/KPF_6$ in MeCN or pivalo-nitrile affords cyclometalated complexes in good yields[10].

Results and Discussion

m-Bromo *N, N*-dimethylbenzylamine was prepared from m-bromotoluene and *N*-Bromo-succinimide using CCl_4 as solvent and benzoyl-peroxide as catalyst followed by addition of *N,N*-dimethylaminei under reflux. The reaction mixture after filtration was chromatographed. Ether: *n*-hexane (1: 4) eluted a yellowish brown band which on evaporation gave yellowish brown oily liquid. The physical parameters of the ligand are given in Table-1.

The physical characteristics of the complexes of *m*-bromo *N, N*-dimethylbenzylamine with Zn (II) and Cd (II) metals are given in Table-2. The complexes are found to be insoluble in THF, DMF, Benzene, and DMSO etc.

Fourier transformed infrared spectra of *m*-bromo *N, N*-dimethylbenzylamine and its complexes showed out of plane aromatic C-H bending bands appeared at 694.1669 cm^{-1}, 775.0018 cm^{-1}, 834.1502 cm^{-1}, 866.9193 cm^{-1}. Inplanei aromatic C-H bending frequencies and bands due to C≡N linkage appeared at 1032.8663 cm^{-1}, 1069.8313 cm^{-1}, 1096.5471 cm^{-1}, 1146.2413 cm^{-1}, 1175.1835cm^{-1}, 1211.8774cm^{-1}. Aromatic C=C stretching bands and stretching bands for methylene in $-CH_2-N$ due to symmetrical vibrations appeared at frequencies 1422.4458 cm^{-1}, 1455.8803cm^{-1}, 1472.4521 cm^{-1}, 1594.6600 cm^{-1}. Bending vibrations for methylene of $-CH_2-N$ appeared at frequencies 2772.3450 cm^{-1} and 2817.9809 cm^{-1}. Absorption bands for $-CH_2-Br$ group appeared at 519.7901 cm^{-1}, 670.30 cm^{-1}, 681.900 cm^{-1}. In case of metal complexes some new bands appeared below 600 cm^{-1} which may be assigned to M-N bond. The lowering in position of bands also depicts the formation of complex [11]. The FTIR data of the ligand and its complexes is given in Table-3.

Table-1: Physical Properties of *m*-Bromo *N,N*-Dimethylbenzylamine

Sr. No.	Physical Properties	Values
1.	Colour	Brownish Yellow
2.	λ_{max}	231.0 nm
3.	Density	1.5 g/ cm^3 at 19 °C
4.	Refractive index	1.549 at 18 °C
5.	Boiling Point	93 °C
6.	Miscibility	Miscible in almost all organic solvents
7.	Viscosity	26.77 poise×10^3 at 18 °C
8.	Surface tension	41.65 Dynes/cm at 18 °C
9.	% age yield	28.1 %

Table-2: Analytical Data and Physical Characteristics of Complexes

Sr. No.	Complexes	Decomposition point	Colour	%age yield
1.	Complex (II)	340 °C	White	12.31 %
2.	Complex (III)	280 °C	White	27.61 %

The atomic absorption data for metal analysis is given in Table-4 which indicates the formation of metal ligand complexes in the ratio of M: L = 1: 1.

Figs. 1 and 2 show the X-ray Diffraction patterns of metal complexes obtained by X-ray diffraction spectroscopy for the determination of crystal structures of complexes. All the complexes were found to be crystalline. All the complexes have primitive Bravice lattice. The crystal system of Zn (II) complex was Rhombohedral and Cd (II) complex was hexagonal. XRD data of complexes is given in Table-5, 6 and 7.

Experimental

E. Merck grade N-Bromosuccinimide, Benzoyli peroxide, Sodium bicarbonate, Carbontetra-chloride, *m*-bromo toluene, *n*-hexane, Silica gel G (type 60), Zinc chloride, Cadmium chloride and NH_3 solution were used in the experimental work. All chemicals were used without further purification.

m-bromo *N,N*-dimethylbenzylamine was prepared by treating m-bromo Toluene with *N*-

Table-3: Fourier Transformed Infrared Data

Sr. No.	Compound No.	Absorption Bands $\bar{\nu}$ (cm^{-1})
1.	Ligand (I)	3060.6299 (w), 2945.6472 (s), 2857.6835(m), 2817.6238 (s), 2772.1932 (s) 1594.6971 (m), 1570.3580 (s), 1472.4470 (s), 1455.9480 (s), 1422.1152 (m) 1358.9980 (m), 1294.7575 (w) , 1249.8869 (w), 1175.2156 (w), 1146.2601 (m) 1096.5306 (w) , 1069.8127 (s), 1032.8442 (m), 997.6202 (w) , 866.9100(m) 834.1383 (m), 775.0507 (s). 694.1242 (s), 670.1911(m)
2.	Complex (II)	3458.3356 (w) , 2926.3195 (w) , 1603.6313(w), 1553.4156 (w), 1507.3532 (s) 1392.418(m), 1122.5542 (w), 1040.9229 (m), 900.3219 (s), 835.4081 (w) 714.8111 (s)
3.	Complex (III)	2925.8357 (m), 2855.1942 (w), 1742.3482(w), 1728.2768 (w), 1711.6895 (w) 1692.4750 (w) , 1621.1154 (s), 1553.5995 (w), 1537.7767(w), 1516.7478 (w) 1503.1584 (w) , 1466.7950 (w) , 1453.0958 (w), 1116.6533 (w), 738.6116(s) 530.6038 (w)

Table-4: Percentage Yield of Metal Estimated by Atomic Absorption Spectroscopy

Sr. No.	Complexes	Theoretical yield	Experimental yield
1.	% age of Zn in Complex (II)	21 %	17.2 %
2.	% age of Cd in Complex (III)	30 %	28.8 %

Table-5: X-Ray Diffraction Analysis of Complex (II)

Peak No.	2θ (Degree)	d-spacing	hkl	Intensity Lin (counts)
1.	16.561	5.34847	1,0,1	680
2.	22.071	4.02412	1,0,4	850
3.	24.819	3.58448	0,1,5	850
4.	28.127	3.17000	1,1,0	800
5.	30.365	2.94130	1,1,3	810
6.	31.045	2.87833	1,0,7	1110
7.	32.815	2.72701	0,2,1	2100
8.	32.482	2.07124	2,0,2	1940
9.	34.416	2.00379	0,1,8	1275
10.	36.333	2.47066	1,1,6	1250
11.	37.857	2.37461	2,0,5	1400
12.	41.527	2.17285	1,0,10	360
13.	43.753	2.06732	2,1,1	325
14.	44.750	2.02357	1,1,0	960
15.	46.328	1.95823	2,1,4	550
16.	47.821	1.90052	1,2,5	480
17.	51.198	1.78282	3,0,3	510
18.	51.642	1.76851	2,1,7	540
19.	54.124	1.69313	2,0,11	740
20.	55.292	1.66011	3,0,6	370
21.	58.155	1.58500	2,2,0	1210
22.	59.433	1.55393	2,2,3	675
23.	61.035	1.51693	0,2,13	640
24.	62.978	1.47473	1,3,4	530
25.	64.198	1.44960	3,1,5	275
26.	64.720	1.43917	2,0,14	340
27.	67.395	1.38841	1,3,7	500
28.	68.729	1.36350	0,4,2	620

bromosuccinimide in CCl_4 using benzoyl peroxide as catalyst under reflux of 8 hours followed by the addition of *N,N*-dimethylamine.The ligand was separated by passing through the column packed with Silica gel G(type 60).

Purity of the iligand was checked by performing TLC. λ_{max} of the Ligand was taken on Hitachi UV-Visible spectrophotometer model U-2800 in CCl_4.

The complexes of the ligand with Zn (II), and Cd(II) metals were synthesized in ethanol : water mixture (2:1). The products were filtered and washed with distilled water, ethanol, ether and n-Hexane and dried to get solid compounds. The melting points or decomposition points were determined on Electrothermal M. P. device model No.1002, USA by keeping the heating rate programmed at 30 ^{0}C per minute. The miscibility of ligand was noted by using common organic solvents.

Table-6: X-Ray Diffraction Analysis of Complex (III)

Peak No.	2θ (Degree)	d-spacing	hkl	Intensity Lin (counts)
1.	17.255	5.13500	0,0,2	1120
2.	27.987	3.18550	1,0,0	420
3.	29.331	3.04250	1,0,1	1450
4.	33.066	2.70694	1,0,2	470
5.	34.918	2.56750	0,0,4	320
6.	38.575	2.33204	1,0,3	1370
7.	45.330	1.99902	1,0,4	200
8.	49.522	1.83915	1,1,0	680
9.	53.004	1.72626	1,0,5	650
10.	59.845	1.59275	2,0,0	80
11.	58.604	1.57393	2,0,1	225
12.	60.843	1.52125	2,0,2	125
13.	61.445	1.50778	1,0,6	150
14.	62.022	1.49514	1,1,4	230
15.	64.473	1.44410	2,0,3	310
16.	69.379	1.35347	2,0,4	70
17.	70.626	1.33260	1,0,7	125
18.	73.745	1.28375	0,0,8	50
19.	75.871	1.25298	1,1,6	200
20.	79.551	1.20401	2,1,0	100
21.	80.621	1.19070	1,0,8	150
22.	82 163	1.17222	2,1,2	60
23.	82.695	1.16602	2,0,6	100
24.	85.406	1.13581	2,1,3	240

Table-7: Crystal Data of Complexes

Complexes	Inter-atomic spacing			Inter-planar Angles			System	Bravice Lattice
	a	b	c	α	β	γ		
Complex (II)	6.34	6.34	23.66	90°	90°	120°	Rhombohedral	Primitive
Complex(III)	3.67	3.67	10.27	90°	90°	120°	Hexagonal	Primitive

FTIR absorption spectra of the ligand and metal complexes were recorded on FTIR spectrophotometer MIDAC Corporation USA model M-2000 series in the spectral range 4000-500 cm^{-1} and resolution of 4 cm^{-1}. The FTIR spectrum of liquid *m*-bromo *N, N*-dimethylbenzylamine was determined as neat by making a thin film between Sodium chloride plates. The FTIR spectra of metal Complexes were taken by pressed disc technique (Sample: KBr = 1 : 100).

Estimation of metals in complexes was carried out on Hitachi Polarized Zeeman Atomic Absorption Spectrophotometer model Z-8000. Crystal structure of the metal complexes was determined by Powder Diffractometer Bruker D8 Discover, Germany.

Synthesis of the Ligand

(m-Bromo N,N-Dimethybenzylamine)

(a) Bromination of m-bromo toluene

m-Bromotoluene (60.652 cm^3, 0.5 mole), *N*-bromosuccinimide (88.9 g. 0.5 mole) and benzoyl peroxide (1.0 g) in CCl_4 (250 cm^3) were charged in a quickfit round bottom flask equipped with water condenser and reaction mixture was heated under reflux for 8 hours, until all the solid started floating on the liquid surface. The mixture was allowed to cool down to room temperature and the regenerated succinimide was filtered off.

(b) Synthesis of m-bromo N, N-dimethylbenzylamine:

m-Bromobenzylbromide (filtrate from step no.1), sodium bicarbonate (42.0 g, 0.5 mole) and distilled water (100 cm^3) were taken in a quickfit round bottom flask (500 cm^3) equipped with water condenser. *N,N*-dimethylamine(52.3 cm^3, 0.5 mole) was added drop wise to the reaction mixture through condenser with the help of separating funnel. The mixture was refluxed for 4 hours. The mixture was then allowed to cool and filtered off. The filtrate was then transferred to a separating funnel where the upper organic layer was collected and passed through a column packed with Silica gel G (type 60). The *n*-hexane: ethanol: ether (5: 2: 1) fraction was collected which on evaporation gave brownish yellow oily

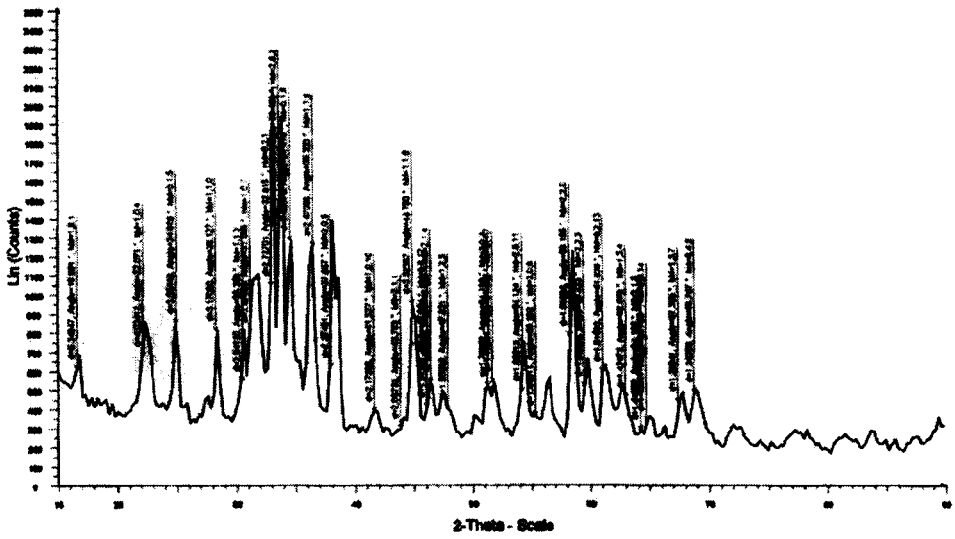

Fig. 1 X-ray Diffraction pattern of Zn (II) complex

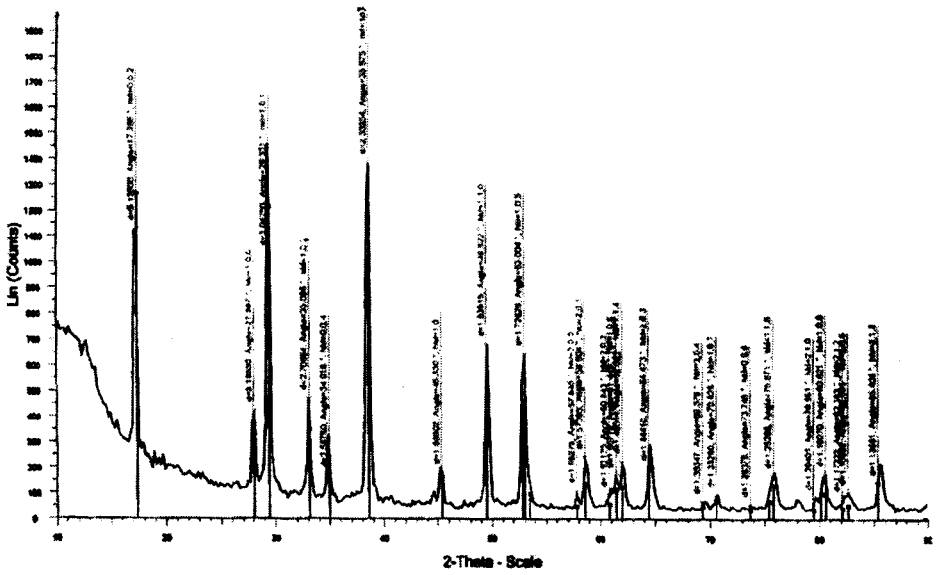

Fig. 2 X-ray Diffraction pattern of Cd (II) complex

liquid (Ligand No.1), soluble in almost all organic solvents.

Formation of Complexes of m-Bromo N,N-Dimethylbenzylamine

(i) Reaction of *m*-bromo *N, N*-dimethylbenzylamine with Zinc chloride ($ZnCl_2$):

m-bromo *N,N*-dimethylbenzylamine (0.85 cm^3, 6.0 mmol) dissolved in ethanol (30 cm^3) was added to Zinc chloride (0.40 g, 3.0 mmol) dissolved in distilled water (15.0 cm^3). The reaction mixture was stirred for 3 hours. A white solid settled which was filtered and washed with distilled water, ethanol, ether and *n*-hexane and dried to get white complex (II).

(ii) Reaction of *m*-bromo *N, N*-dimethyl-benzylamine with Cadmium chloride ($CdCl_2$):

m-bromo N, N-dimethylbenzylamine (0.85 cm^3, 6.0 mmol) dissolved in ethanol (30 cm^3) was added to Cadmium chloride (0.55 g, 3.0 mmol) dissolved in distilled water (15.0 cm^3). The reaction mixture was stirred for 3 hours. A white solid settled which was filtered and washed with distilled water, ethanol, ether and *n*-hexane and dried to get white complex (III).

Conclusions

m-Bromo *N, N*-dimethylbnenzylamine, a brownish yellow liquid acts as a bidentate ligand in the formation of stable complexes with Zn (IIB) and Cd (IIB) metals. λ_{max} of m-bromo *N, N*-dimethyl-benzylamine was determined to be 231.0 nm. The complexes were insoluble in almost all organic solvents. FTIR spectroscopic analysis of the ligand and its complexes confirmed the formation of complexes. Atomic Absorption Spectroscopic analysis of complexes revealed the metal ligand ratio of complexes to be M: L=1: 1. X-ray Diffraction analysis of the complexes showed that they were crystalline in nature.

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