Synthesis of Ortho-Nitro-N,N′-Dimethylbenzylamine Derivatives of Group I (b) and II (b) Metals

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Summary: Derivatives of *o*-Nitro-N,N'-dimethylbenzylamine with group I (b) and II (b) metals were synthesised and characterized. The proposed formulae are based on the analytical data, chemical characteristics and spectroscopic evidence. The compounds are very stable, crystalline in nature and are obtained in high yield.

Introduction

It has been reported [1-8] that nitrogen containing organic bases react with transition metals to give derivatives in which ligand is chelated to metal *via* nitrogen electron pair and simultaneous formation of M-C σ bond to the carbon of phenyl ring.

N,N′-dimethylbenzylamine reacts with group 1 (b) and II (b) metals to give crystalline derivatives in high yield. These products are stable and insoluble in most of the organic solvents [9]. Similarly group I (b) and II (b) metals reacts with *o*-cyano N,N′-dimethylbenzylamine to give high yield of crystalline products [16]. The infrared spectra of derivatives of group I (b) and II (b) metals with N,N′-dimethylbenzalamine and *o*-cyano N,N′-dimethylbenzylamine were observed between 855-710 cm^{-1} which indicate M-N stretching vibration in relatively lower frequency region as expected [9-16].

Formation of chelates of group I(b) and II (b) with N,N′-dimethylbenzylamine and *o*-cyano N,N′-dimethylbenzylamine [16] as well as their scope to describe the mechanism of reaction invited the attention of authors to study derivatives of *o*-nitro N,N′-dimethylbenzylamine with group I (b) and II (b) metals.

Results and Discussion

The synthesis of orhto-nitro substituted derivatives of N,N′-dimethylbenzylamine has already been reported [9]. The ortho substituted derivative which carries electron withdrawing group ($-NO_2$) weakens the C-H bond to a large extent. When a transition metal in its normal oxidation state is allowed to react with this ligand, metal ligand bond (M-N) is established easily through nucleophilic attack of the ligand nitrogen on the transition metal. This results in the directive influence of metal on the ortho carbon of the benzene ring which forms a metal carbon bond at the ortho position and ultimately gives stability to the complex through cyclization, similar to the derivatives already reported [9-16].

The IR spectrum of *o*-nitro N,N′-dimethylbenzylamine indicates C-H stretching frequency of unsaturated bond at 3100-3000 cm^{-1}, C-H stretching frequency of CH_3, $-CH_2-$ and of benzene ring are observed at 2950 cm^{-1} and 2850-2800 cm^{-1} respectively. The characteristic stretching frequency of C-N bond of $(CH_3)_2$ N-type is indicated at 1280-1180 cm^{-1}. N-C stretching frequency of nitro-aryl is characteristically observed at 1590-1460 cm^{-1}. Aromatic ring deformation and bending vibrations are indicated at 1100-1040 cm^{-1}. Formation of M-N bond in complexes of I(b) and II (b) group metals with *o*-nitro N,N'-dimethylbenzyl-amine was observed in the IR region between 810-730 (Table 3) as expected [10,11]. The lowering of M-N stretching frequency in all the metal derivatives indicates complex formation through co-ordinate bond. These complexes are highly stable through cyclometalation. On the basis of compounds already reported [14,16] intramolecular C-H oxidative addition is expected in which C-H bond breaking and M-C bond formation occurs simultaneously (SN_2) for aryl group attached to coordinate nitrogen ligand.

Experimental

a) BDH/E. Merck chemicals were used after further purification and solvents were distilled before use.

b) 66 per cent absolute ethanol and 34 per cent water mixture was used as a solvent in various reactions.

c) Ortho-nitro N,N'-dimethylbenzylamine was synthesized as reported earlier [9].

d) The metal contents of the complexes were estimated following the standard procedure with "Varian -AA-1275" Atomic Absorption Spectrophotometer after digestion of known amounts of samples in conc. HNO_3.

e) IR spectra of complexes were recorded with KBr pellet on "Hitachi 270-30" Infrared spectrophotometer. IR spectra of *o*-nitro N,N'-dimethylbenzylamine was taken in thin film.

Reaction of o-nitro, N,N'-dimethylbenzylamine with copper (II) chloride

$CuCl_2.2H_2O$ (1.705g, 10 m.mol) was dissolved in ethanol (30 cm^3) poured into a three necked flask, equipped with water condenser and stirring arrangement. *o*-Nitro N,N'-dimethylbenzylamine (1.34 g, 20 m.mol) was added dropwise and the reaction mixture was stirred for three hours. Brown like amber coloured crystals settled down. They were centrifuged, washed three times with *n*-hexane (15 cm^3), dried at room temperature to get complex-I (3.845 g). Physical and analytical data are given in Table 1, 2 and 3.

Table 1: Physical data of compounds formed by reaction of *o*-nitro N,N'-dimethylamine with I(b) and II(b) group metals

Complex	Colour	%age yield	m.p.	Solubility
I	Brown like amber	90.8	144 °C	Insoluble in Hexane, Chloroform; 1,2 dichloro ethane, T.H.F.
II	Black	55.0	above 300 °C	-do-
III	White	69.1	above 300 °C	-do-
IV	White	84.5	234 °C	-do-
V	White	73.2	217 °C	-do-
VI	Greenish Grey	54.0	241 °C	-do-

Reaction of o-nitro, N,N'-dimethylbenzylamine with silver (I) nitrate

$AgNO_3$ (0.8493 g, 5 m.mol) in ethanol (20 cm^3) was transferred to a three necked flask, equipped with water condenser and stirring arrangement *o*-nitro N,N'-dimethylbenzylamine (1.34 g, 10 m. mol) was added dropwise in the flask and the reaction mixture was stirred for three hours. Black coloured crystals separated out. They were centrifuged, washed three times with *n*-hexane (15 cm^3) and dried at room temperature to afford complex-II (2.27 g). Physical and analytical data of the compound are given in Table 1, 2 and 3.

Reaction of o-nitro N,N'-dimethylbenzylamine with gold (III) chloride

$NaAuCl_4.2H_2O$ (0.07 g, 0.2 mmol) in ethanol (20 cm^3) was taken in a three necked flask, fitted with water condenser and stirring arrangement, *o*-nitro N, N'-dimethylbenzylamine (1.34 cm^3, 10 m. mol) was poured dropwise into the flask and the reaction mixture was stirred for three hours. Black coloured crystals were separated with the help of centrifugal machine, washed three times with *n*-hexane (15 cm^3) and dried at room temperature to get complex-III

Table 2: Analytical data

Complex	Formula	% age of metal Theoretical	Experimental
I	$[Cu_2(C_9H_{11}N_2O_2)_2\,Cl_2]$	22.84	23.02
II	$[AgC_9H_{11}N_2O_2]NO_3$	37.57	37.37
III	$[Au_2(C_9H_{11}N_2O_2)_2Cl_2]Cl_2$	44.07	44.01
IV	$[Zn_2(C_9H_{11}N_2O_2)_2Cl_2]$	23.36	23.62
V	$[Cd_2(C_9H_{11}N_2O_2)_2\,Cl_2]$	34.38	34.37
VI	$[Hg_2(C_9H_{11}N_2O_2)_2\,Cl_2]$	48.32	47.87

Table 3: Infrared spectra

Complex	Ligand/ Metals with Oxidation State	$\nu_{max}CM^{-1}$
-	$C_9H_{12}N_2O_2$	3100 (ms), 3000 (ms), 2950 (s), 2850 (ms), 2840 (ms), 2770 (ms), 1620 (s). 1460(s), 1360 (s) 1300 (ms), 1160 (ms).
I	Cu(II)	2950 (s), 2870 (s), 1540 (s), 1467 (s), 1380(s), 1350 (s), 1220 (w), 750 (s).
II	Ag(I)	2975 (s), 2900 (s), 1480 (s) 1400 (s), 1180 (w), 740 (ms).
III	Au (III)	2950 (s), 2875 (s), 1470 (s), 1390 (s), 1170 (w), 730 (s).
IV	Zn(II)	2900 (s), 2850 (s), 1470 (w), 1390 (s), 1140 (w), 730 (s).
V	Cd (II)	2950 (s), 2875 (s), 1470 (s), 1380 (s), 1170 (w), 740 (s).
VI	Hg(II)	2950 (s), 2875 (s), 1470 (s), 1390 (s) 1170 (w), 810 (s).

(0.076 g). Physical and analytical data of the compound are given in Table 1, 2 and 3.

Reaction of o-nitro N,N'-dimethylbenzylamine with zinc (II) chloride

$ZnCl_2$ (0.681, 5 m.mol) in ethanol (20 cm^3) was transferred to a three necked flask, equipped with water condenser and stirring arrangement, *o*-nitro N,N'-dimethylbenzylamine (1.34 g, 10 m.mol) was poured into the flask with constant stirring for three hours, white needle like crystals appeared. These were centrifuged, washed three times with *n*-hexane (15 cm^3) and dried at room temperature to afford complex-IV (3.30 g). Physical and analytical data of the compound are recorded in Table 1, 2 and 3.

Reaction of o-nitro N,N'-dimethylbenzylamine with cadmium (II) chloride

$CdCl_2$. $2.5H_2O$ (1.141 g, 5 m.mole) in (30 cm^3) was transferred to a three necked flask which was fitted with water condenser and stirring arrangements *o*-nitro N,N'-dimethylbenzylamine (1.34 g, 10 m. mole) was added in the flask. The reaction mixture was stirred for three hours. White crystals separated out. These were centrifuged, washed three times with *n*-hexane (15 cm^3) and dried at room temperature to get complex-V (3.040 g). The physical and analytical data of the compound are reported in Table 1, 2 and 3.

Reaction of o-nitro N,N'-dimethylbenzylamine with mercury(II) chloride

$HgCl_2$(1.357 g, 5 m.mole) was dissolved in (30 cm^3) of ethanol and transferred to a three necked flask, equipped with water condenser and stirring arrangement *o*-nitro N,N'-dimethylbenzylamine (1.34 g, 10 m.mole) was poured dropwise into the flask. The reaction mixture was stirred for three hours, and black crystals appeared. These were centrifuged, washed three times with *n*-hexane (15 cm^3) and dried at room to get complex-VI (2.487 g). Physical and analytical data of the compound are given in Table 1, 2 and 3.

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