# Benzylideneaniline and N,N'-Dimethylbenzylamine Derivatives of I(b) and II(b) Metals

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**Summary:** Benzylideneaniline and N,N'-dimethylbenzylamine derivatives of I(b) and II(b) metals are reported. The proposed formulae are based on their analytical data, chemical characteristics and spectroscopic evidence. The compounds are well defined solids and fairly stable. Fusion with Lewis bases results in bridge cleavage reactions.

## Introduction

Some of the transition metal derivatives containing organic ligands undergo intramolecular metalation. Cyclometalation [1] reactions have been described in terms of their scope, mechanism and utility in organic syntheses. Although, cyclometalated derivatives of transition metals have been studied in some detail but only a few scattered reports [2-4] of the derivatives of group I(b) and II(b) metals are available in literature. Stable aryl copper compounds containing 2-(dimethylamino) methyl and 2-(methoxy methyl) groups attached to the aryl groups have been prepared from organolithium compounds and cuprous bromide [2]. Aryl bridged tetranuclear copper-lithium cluster compounds have been synthesized and characterized [3].

Similarly, 2-(Dimethylamino) methyl phenyl silver was prepared from 2-(Dimethylamino) methyl phenyllithium and silver-bromide [3]. Tetranuclear, mixed metal clusters containing aryl groups, bridging the silver and lithium metals are also reported [4].

Formation of chelates derived from Schiff's bases in aqueous, dioxane [5] and non-aqueous solvents [6] is described. Such and other related reactions prompted us to study the derivatives of N,N'-dimethylbenzylamine and benzylideneaniline with group I(b) and II(b) metals.

## Experimental

Solvents were redistilled and compounds recrystallised prior to their use. Melting points were taken on Gallenkamp melting point apparatus. Infrared spectra were taken in Nujol mull on Beckman's Acculab 10 Infrared Spectrophotometer and are given in Table 1. The complexes were analysed for metal [7] colorimetrically using photoelectric colorimeter K Fuji Model F-10 and halogens by Stempanow method [8]. Nitrogen was estimated by Kjeldahl's method.

*Reactions of N,N'-Dimethylbenzylamine I) With Copper(II) Acetate:*

A solution of N,N'-dimethylbenzylamine (4.056g, 30.00 m mole) in 20.00 ml ethanol-water (1:1) was

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added slowly to a solution of copper (II) acetate (1.816g, 10.0 m mole) in 20.0 ml. ethanol-water (1:1) and solution stirred for 2h at room temperature. A pale green solid settled which was washed with ethanol and subsequently with n-hexane to get complex (I), sparingly soluble in T.H.F. and benzene (1.3g, 40.3%; m.p. 138-142°d; $C_{18}H_{26}N_2$ Cu, (%) Cu: Calc. 19.0, Exp. 19.1 : N (%) Calc. 8.39, Exp. 8.41.

*II) With Copper(II) Chloride:*

A solution of copper (II) chloride (1.70g; 10.00 m mole) in 10.00 ml ethanol was added to N,N'-dimethylbenzylamine (4.956g, 30.0 m mole) in ethanol (10.00 ml.) and stirred for 2h at room temperature to get deep green solid of complex (II) which was filtered and washed with ethanol and subsequently with n-hexane and was insoluble in most of the organic solvents (1.5g, 64.7%; M.P. 175°d; Based on $C_9H_{13}NClCu$, (%) Cu: Calc. 27.1 Exp. 28.8%, Cl: Calc. 15.1, Exp. 15.0, (%) N: Calc. 5.98, Exp. 6.01).

*(III)With Silver (I) Nitrate:*

A solution of silver (I) nitrate (1.698g, 10.0 m mole) in 10.0 ml ethanol-water (1:1) was added to N,N'-dimethylbenzylamine (4.056g, 30.0 m mole) in 10.0 ml. ethanol-water (1:1) and stirred for 2h at room temperature. The reaction was carried in Amber glass flask in order to keep it away from direct sun-light. Dark brown solid of complex (III) settled which was filtered and washed with ethanol and n-hexane (1.0g, 33.3%; m.p. above 300°d; based on $C_{18}H_{26}N_2Ag$ (%) Ag: Calc. 28.5, Exp. 28.4; (%) N: Calc. 7.39, Exp. 8.02).

*(IV) With Gold (III) Chloride:*

To a solution of gold (III) chloride of (0.909g, 3.0 m mole) in 10.0 ml ethanol was added, N,N'-dimethylbenzylamine (1.217g, 9.0 m mole) in 10.0 ml of ethanol and stirred at room temperature for 3 hours to get nice orange yellow crystals which were washed with ethanol to get complex (IV) (1.1g, 99.9%; M.P. 165°d; Based on $C_9H_{13}NClAu$, (%) Au: Calc. 53.6, Exp. 52.0; (%) Cl: Calc. 9.6, Exp. 9.2; (%) N: Calc. 3.81, Exp. 3.80).

*(V) With Zinc (II) Chloride:*

Addition of N,N'-dimethylbenzylamine (1.217g, 9 m mole) in 30.0 ml ethanol-water (1:1) to a solution of zinc (II) chloride (0.408g, 3.0 m mole) in 30.0 ml ethanol-water (1:1) and stirring at room temperature for 0.5 h gave white precipitate. The white solid was recrystallised from tetrahydrofuran and washed with petroleum ether and n-hexane to get complex (V) (0.5g, 71.42%; M.P. 240°d; based on $C_9H_{13}NClZn$, (%) Zin: Calc. 27.6; Exp. 28.0; (%) Cl: Calc. 15.0, Exp. 14.9; (%) N: Calc. 5.95, Exp. 5.90).

*(VI) With Cadmium (II) Chloride:*

On adding N,N'-dimethylbenzylamine (1.27g, 9.0 m mole) in 30.0 ml ethanol-water (1:1) to a solution of cadmium (II) chloride (0.549, 3.0 m mole) in 30.0 ml ethanol-water (1:1) a white crystalline solid settled. The solution was stirred for 0.5 h at room temperature. The complex (VI) was obtained, purified by recrystallisation from T.H.F. as white solid (0.7g, 83.33%; M.P. 260°d; based on $C_9H_{13}NCl$ Cd (%) Cd: Calc. 47.2, Exp.

46.7; (%) Cl: Calc. 14.9 Exp. 14.3; (%) N: Calc. 3.93, Exp. 3.89).

*(VII) With Mercury (II) Chloride:*

To a solution of mercury (II) chloride (0.814g, 3m mole) in 30.0 ml ethanol-water (1:1) was added N,N'-dimethylbenzylamine (1.217 g, 9.0 m mole) in 30.0 ml ethanol water (1:1). A bright yellow solid settled immediately. The solution was stirred for 0.5h at room temperature and filtered when an orange yellow complex (VII) was obtained which was washed with T.H.F. and n-hexane (1.3g, 86.66%; M.P. 190°d; based on $C_9H_{13}NCl$ Hg (%) Hg: Calc. 54.0, Exp. 53.7; (%) Cl: Calc. 9.5, Exp. 9.2, (%) N: Calc. 3.77; Exp. 3.72).

*Reactions of Benzylideneaniline*

*(I) With Copper (II) Chloride:*

A solution of copper (II) chloride (1.70 g, 10.0 m mole) in 10.0 ml of ethanol was added to benzylideneaniline (1.81g, 10.0m mole) dissolved in 10.0 ml of ethanol and solution stirred for 3h at 30°C to get a deep brown solid which was washed with ethanol and subsequently with diethyl ether and petroleum ether to get complex (VIII), sparingly soluble in T.H.F. and DMSO. (1.6g, 57.3%; M.P. 130°d; based on $C_{13}H_{11}ClCu$, (%) Cu: Calc. 22.6, Exp. 22.4; (%) Cl: Calc. 12.6, Exp. 12.4; (%) N: Calc. 5.00; Exp. 4.92).

*(II) With Gold (III) Chloride:*

A solution of gold (III) chloride (0.909g, 3.0 m mole) in 10.0 ml of ethanol was added to benzylideneaniline (0.543g, 3.0 m mole) taken in 10.0 ml ethanol and solution stirred for 24h at room temperature. A yellow crystalline solid settled which was recrystallised from DMSO and washed with petroleum ether to get complex (IX) (0.5 g, 40.65%; M.P. 217°d; based on $C_{13}H_{11}ClAu$; (%) Au: Calc. 47.7; Exp. 46.9; (%) Cl: Calc. 8.5, Exp. 8.2; (%) N: Calc. 3.38; Exp. 3.35).

*(III) With Zinc (II) Chloride:*

Addition of benzylideneaniline (5.43g, 30 m mole) in 30.0 ml of ethanol to solution of zinc (II) chloride (4.08g, 30 m mole) in 30.0 ml of ethanol and stirring at 35-40°C for one hour gave off-white small crystals of complex (X). The complex was washed with petroleum ether and recrystallised from acetone (2.0g, 21.07%; m.p. 245°d; based on $C_{13}H_{11}NClZn$, (%) Zn: Calc. 23.1, Exp. 22.9; (%) Cl: Calc. 12.5, Exp. 12.4; (%) N: Calc. 4.96; Exp. 4.95).

*(IV) With Cadmium (II) Chloride:*

Adding benzylideneaniline (5.43g, 30mmole) in 50.0 ml of ethanol to a solution of cadmium (II) chloride (5.43g, 30.0 m mole) in 60.0 ml of ethanol and stirring for 3.0 h at 35-40°C gave white fluffy crystals of complex (XI) which was purified by washing with petroleum ether and recrystallising from acetone (8.0g, 82.47%; M.P. 295°d; based on $C_{13}H_{11}NClCd$, (%) CD: Calc. 34.01, Exp. 34.0; (%) Cl: Calc. 10.7, Exp. 10.6; (%) N: Calc. 4.25; Exp. 4.20).

*(V) With Mercury (II) Chloride:*

To a solution of mercury (II) chloride (8.14g, 30.0 m mole) in 60.0 ml of ethanol was added benzylideneaniline (5.43g, 30.0 m mole) in 60.0 ml of ethanol. The solution was stirred

for 24h at room temperature when light yellow crystals settled. The yellow crystalline product was washed with petroleum ether and recrystallised with acetone to get complex (XII) (5.0g, 40.0%; M.P. 135-140°d; based on $C_{13}H_{11}NClHg$, (%) Hg: Calc. 48.0, Exp. 48.0; (%) Cl: Calc. 8.5, Exp. 8.0; (%) N: Calc. 3.35, Exp. 3.39).

*Reactions of Complex (V)*

*(a) With triphenylphosphine:*

The complex (V) (0.1g) and triphenylphosphine (0.2g) were fused at 40°C and melt thus obtained was dissolved in hot T.H.F. On cooling the solution off-white crystals of complex (XIII) were obtained. Recrystallisation with acetone gave off-white crystals (0.25g, m.p. 105°C).

*(b) With p-Toluidine:*

The complex (V) (0.1g) and p-toluidine (0.2g) were well mixed and fused to get a melt which was dissolved in hot DMSO and cooled to get buff crystals of complex (XIV) which were washed with petroleum ether and recrystallised with acetone (0.15g, m.p. 180°d (M. Wt. (Calc.) based on $C_{16}H_{22}N_2ClZn$; 342, Obs. Osmometrically in benzene, 352).

*Reaction of Complex (VII)*

*(a) With triphenylphosphine:*

The complex (VII) (0.1g) and triphenylphosphine (0.2g) were fused at 40°C and the melt thus obtained was washed with ethanol and acetone to get complex (XV) as gray solid (0.04g; M.P. 190°d).

*(b) With p-Toluidine:*

A mixture of complex (VII) (0.1g) and p-toluidine (0.2g) were fused to get a green melt. The melt was dissolved in hot DMSO and cooled to get buff solid which was washed with acetone to get the complex (XVI) (7.mg; m.p. 170°d).

*(c) With Pyridine:*

The complex (VII) (0.1g in pyridine 2.0 ml) was heated to boiling for 2h to get a clear solution which on cooling gave dark yellow crystalline solid. The yellow solid was dissolved in minimum volume of hot DMSO and cooled to get yellow crystals of complex (XVII) 6 mg; 180°C, (M. Wt. (Calc.) based on $C_{14}H_{18}N_2ClHg$, 450, Osmometrically in benzene, 462).

*Reactions of Complex (XI)*

*(a) With triphenylphosphine:*

Addition of complex (XI) (0.1g) in DMSO (5 ml) to a solution of triphenylphosphine (0.2g) in DMSO (5 ml) and stirring at 40°C for 0.5h and on cooling, yellow crystals were obtained which were washed with petroleum ether and recrystallised with acetone to get the complex (XVIII) (0.070g; m.p. 156°C).

*(b) With p-Toluidine:*

Addition of p-toluidine (0.2g) in methanol (10.0 ml) to a solution of complex (XI) (0.1g) in methanol (10.0 ml) and stirring at 20°C for 1h and then cooling for three hours gave silver white crystals which were washed with petroleum ether and recrystallised with acetone to get the complex (XIX) 0.080g; M.P. 190°d).

*(c) With Pyridine:*

Addition of complex (XI) (0.25g) in methanol (20.0 ml) to pyridine (5.0 ml) in methanol (20.0 ml) and stirring at room temperature for 0.5 h gave white solid which was filtered and

Table-1: Infrared Data

| Compound | Wave No. ( $\nu$ ) $Cm^{-1}$ |
|---|---|
| Complex (I) | 3520w, 3390w, 3260, 1550s, 1410s, 1340w, 1020m, 800m, 720w, 665w, 650w. |
| Complex (II) | 3440w, 3350m, 980w, 845m, 695w, 600m. |
| Complex (III) | 1570w, 600vw. |
| Complex (IV) | 3520s, 3460m, 3050w, 2740m, 1590m, 1430, 1350w, 1230m, 1170m, 1060w, 1010m, 960m, 930m, 835, 800m, 745s, 710m, 600s. |
| Complex (V) | 3520vs, 3450sh, 1600w, 1040w, 905ms, 730sh, 720s. |
| Complex (VI) | 3520vs, 740ms. |
| Complex (VII) | 3150w, 2740w, 1640ms, 1200w, 1115w, 1090sh, 1065m, 1015m, 925m, 835m, 795m, 735s, 690s. |
| Complex (VIII) | 3220w, 1600sh, 1560m, 1490w, 1300m, 1240m, 1150m, 800w, 750w, 690w. |
| Complex (IX) | 3149s, 3060s, 1705m, 1595s, 1580m, 1560m, 1480s, 1405w, 1330w, 1285w, 1245m, 1200m, 1185m, 1160w, 1080m, 1030m, 1020m, 1000w, 830m, 770s, 740s, 730w, 680s. |
| Complex (X) | 3450w, 3260s, 3220m, 3130ms, 3040m, 1600s, 1575s, 1490s, 1220ms, 1145m, 1110vs, 1070ms, 1025m, 1000w, 960w, 900m, 800m, 755vs, 690vs, 670m, 655sh, 465m. |
| Complex (XI) | 3530m, 3470w, 3420sh, 3320s, 3250ms, 3150m, 3040m, 2720w, 1930w, 1850w, 1720w, 1600s, 1585ms, 1500s, 1240m, 1230sh, 1185ms, 1070m, 1040s, 1010s, 995ms, 900w, 880w, 805ms, 750vs, 690s. |
| Complex (XII) | 3230m, 3160ms, 3090m, 1595m, 1565s, 1485s, 1265m, 1140m, 1070m, 1025m, 900w, 800w, 755s, 685ms. |
| Complex (XIII) | 3060m, 1580w, 1432s, 1305w, 1200m, 1175sh, 1150ms, 1120s, 1090m, 1070m, 1025m, 1000m, 850ms, 750ms, 720ms, 690s. |
| Complex (XIV) | 3490s, 3450sh, 3330m, 1720w, 1600w, 1260w, 1240m, 1040w, 910m, 725ms. |
| Complex (XV) | 3050wm, 1480sh, 1334ms, 1305w, 1185m, 1160w, 1120w, 1100m, 1070w, 1030w, 995m, 745m, 720m, 710sh, 690ms. |
| Complex (XVI) | 3450w, 3360w, 3090w, 1505w, 1270w, 1200m, 1110w, 1045w, 890w, 825ms, 770w, 750w, 720w, 610w. |
| Complex (XVII) | 2600m, 1720w, 1600w, 1540w, 1490ms, 1400sh, 1350sh, 1320w, 1145s, 1090s, 1039m, 970w, 805m, 790s, 735m, 720w, 690m, 640w, 610m. |
| Complex (XVIII) | 3460w, 3660m, 1620w, 1580w, 1475s, 1430s, 1310m, 1200sh, 1170m, 1120m, 1095m, 1070sh, 1025m, 995ms, 940m, 905w, 800w, 745s, 725m, 710sh, 690s, 610w. |
| Complex (XIX) | 3100w. 3050w, 3030m, 3000sh, 1700w, 1635w, 1600w, 1570m, 1485ms, 1450vs, 1360m, 1325w, 1235m, 1220ms, 1155ms, 1080s, 1035s, 1010s, 950w, 880w, 750s, 690vs, 675w, 665m, 630ms. |
| Complex (XX) | 3320ms, 3260ms, 3030m, 1620w, 1600w, 1580m, 1515ms, 1240ms, 1155w, 1115sh, 1100m, 1040s, 1020sh, 935w, 840w, 810ms, 740w, 705w. |

Table-1: cont'd.

| Compound | Wave No. ( $\nu$ ) $Cm^{-1}$ |
|---|---|
| Complex (XXI) | 3070sh, 3050m, 1585w, 1570w, 1480w, 1435s, 1330w, 1310m, 1280w, 1185m, 1160m, 1100s, 1070m, 1030m, 1100ms, 760s, 750s, 710s, 695s, 615w. |
| Complex (XXII) | 2680w, 1590w, 1570w, 1480s, 1435s, 1330w, 1315m, 1290w, 1185m, 1160m, 1100vs, 1070m, 1030ms, 1000s, 930w, 860m, 760sh, 720s, 700vs, 620w, 505s. |
| N,N'dimethylbenzyl-amine. | 3070w, 3040m, 2780ms, 1495m, 1365ms, 1260m, 1175m, 1150m, 1100w, 1080w, 1045m, 1035sh, 1030s, 980w, 915w, 850ms, 740s, 700s, 610w, 570w. |
| Benzylideneaniline | 3060w, 3020w, 1625ms, 1590ms, 1575sh, 1375sh, 1365m, 1310w, 1190ms, 1170ms, 1155sh, 1070m, 1025m, 990w, 975m, 905m, 875m, 765s, 695vs, 540m. |

m=medium, ms=medium strong, sh=shoulder, vs=very strong

vw=very weak, w=weak.

washed with petroleum ether to get the complex (XX). The complex was recrystallised with acetone (0.20g), M.P. 245°d (M. Wt. (Calc.) based on $C_{18}H_{16}N_2ClCd$, 361, Obs. Osmometrically in benzene 368).

*Reactions of Complex (XII)*

*(a) With triphenylphosphine:*

Addition of complex (XII) (0.1g) in T.H.F. (10 ml) and triphenylphosphine (0.2g) in T.H.F. (10.0 ml) and stirring at room temperature for 1h gave white fluffy crystals which were washed with petroleum ether and recrystallised with acetone to get the complex (XXI) (0.060g; m.p. 260°d).

*(b) With Pyridine:*

Addition of pyridine (2.0 ml) in T.H.F. (5.0 ml) to complex (XII) (0.1g) in T.H.F. (5.0 ml) and stirring at room temperature for 3h gave white crystals after allowing to stand overnight. The crystals were washed with petroleum ether and recrystallised with DMSO to get the complex (XXII) as white long prismatic crystals (280mg, M.P. 200°d; (M. Wt. (Calc.) based on $C_{18}H_{16}N_2ClHg$, 496, Obs. Osmometrically in benzene 504).

## Results and Discussion

N,N'-dimethylbenzylamine reacts with group I(b) metals to give coloured complexes. Copper (II) acetate reacts with N,N'-dimethylbenzylamine to give a pale green complex in 40% yield and is sparingly soluble in benzene and T.H.F. Its infrared spectrum indicates a characteristics medium strong band at 800 $cm^{-1}$ and C-N stretching at 1340 $cm^{-1}$.

Copper (II) chloride reacts with N,N'-dimethylbenzylamine to give a deep green complex in more than 64% yield and with slightly higher melting range. Infrared spectrum shows a medium strong band at 845 $cm^{-1}$. Benzylideneaniline also reacts with copper (II) chloride to give a deep brown solid of complex (VIII) in

slightly lower yield and melting range. Infrared spectrum has shown medium strong band at 800 $cm^{-1}$, C-N stretching at 1500 $cm^{-1}$, 1240 $cm^{-1}$, 1300 $cm^{-1}$, [11], and C-C stretching of aromatic ring around 1560 $cm^{-1}$.

Silver (I) and gold (III) Chloride also react with N,N'-dimethylbenzylamine and benzylideneaniline to give stable complexes. Surprisingly, the silver (I) complexes have melting range higher than those of copper (II) and gold (III) complexes. The Ag(I) complexes are brown and gold (III) derivatives are nice yellow crystals but insoluble in most of the organic solvents except DMSO. The infrared spectra show medium strong band around 800 $cm^{-1}$, C-N stretching at 1590 $cm^{-1}$, 1060 $cm^{-1}$, 1170 $cm^{-1}$ [11], C-C stretch of aromatic ring at 1590 $cm^{-1}$ [11].

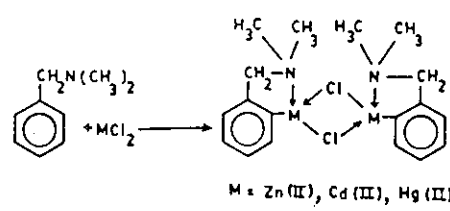
Group II(b) metals react under room temperature conditions with N,N'-dimethylbenzylamine and benzylideneaniline to get fairly high yields of products. Zinc (II) derivatives are obtained in high yields as white crystalline solids and are fairly stable. The infrared spectra give medium bands at 730 $cm^{-1}$, C-N stretching at 1040 $cm^{-1}$ [11], C-C stretch of aromatic ring around 1600 $cm^{-1}$ [11].

Cadmium (II) derivatives of N,N'-dimethylbenzylamine and benzylideneaniline are also obtained as white crystalline solids with yields higher than 80%. These complexes are sparingly soluble in polar organic solvents and their infrared spectra indicate characteristic medium strong band at 805 $cm^{-1}$.

The mercury (II) derivatives of N,N'-dimethylbenzylamine and benzylideneaniline are relatively unstable but could be prepared as yellow crystalline solids, insoluble in most of the polar organic solvents. Characteristic band at 835 $cm^{-1}$ alongwith C-N stretch at 1375 $cm^{-1}$ appeared.

It has been reported [12-15] that azobenzene, N,N'-dimethylbenzylamine and benzylideneaniline react with transition metals to give complexes in which ligand chelate to metal via the nitrogen electron loose pair and M-C, σ-bond to the carbon of phenyl ring i.e. the metal is ligand C, N-bonded.

The wide range of C,N-complexes have been reported [13-15] with the transition metals of group (VIII). The derivatives of N,N'-dimethylbenzylamine and benzylideneaniline obtained with metals of group (II) are now reported as C,N-bonded complexes. The bridge cleavage reactions with strong ligands (L = triphenylphosphine, pyridine, p-toluidine etc.), have resulted in the formation of monomeric species as indicated osmometrically. Bridge cleavage reactions of N,N'-dimethylbenzylamine with halides of Zn(II) Cd(II) and Hg(II) can be represented as:




Comparing the infrared spectra of complexes of N,N'-dimethylbenzyl and benzylideneaniline and I(b) and II(b) group metals with those of cyclometallated complexes reported [13-15], a supporting evidence is obtained in

favour of cyclometalation in view of similarity in IR bands in the region 1600-1570 $cm^{-1}$.

It has been reported that Co-N IR Frequency appears around 820 $cm^{-1}$ and change in the anion causes a slight shift in this position. Report on the measurement of absorption spectra of Cr(III) and Ni(II) complexes have indicated that M-N IR band should appear at 786 $cm^{-1}$ and 830 $cm^{-1}$, respectively [10]. The observed IR frequencies of Fe-N reported at 745 $cm^{-1}$ and theoretical band assignment based on Fe-N stretching force constant 4.7 x $10^5$ dynes/cm is 756 ($A_2$) $cm^{-1}$ 742 $cm^{-1}$ (E) [16].

The M-N stretching frequency is of special interest because it provides useful information about the coordinate bond. Because of the selectively heavy mass of metal and due to low bond order of the coordinate bond, the M-N stretching vibration appears in the lower frequency region. Some workers [10] have suggested the M-N bond between 850 $cm^{-1}$ and 650 $cm^{-1}$ in metal amine complexes. Powell and Sheppard have indicated [16] that a relationship exists between stability and M-N stretching frequency and it may appear well below 800 $cm^{-1}$. We have also observed M-N IR band in complexes of I(b) and II(b) group metals with M,N'-dimethylbenzylamine in the region between 835-710 $cm^{-1}$ as expected. Similarly benzylidene-aniline derivatives show IR bands in the region 830-720 $cm^{-1}$.

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