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^{1}H, ^{13}C and ^{199}Hg NMR Characteristics of New Amine–Mercuric Chloride Complexes

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Abstract

Reduction of some *N*-alkylimines has been achieved with $NaBH_4$ to give the corresponding secondary amines with high yields (85–95%). These amines were characterized on the bases of their ^{1}H and ^{13}C NMR spectra. The reaction of these amines with mercuric chloride to afford the corresponding complexes was found to occur through a weak dative bond between the nitrogen lone pair of electrons and the mercury atom to form $HgCl_2L_2$ complexes. The ^{1}H, ^{13}C and ^{199}Hg NMR chemical shifts have been obtained as well as $^{1}J(^{13}C–H)$ and $^{2}J(^{13}C–H)$ coupling constants. Labelling with nitrogen-15 revealed that there is a weak coupling between the nitrogen and the ^{199}Hg.

Introduction

In the last few years, considerable efforts have been devoted to the ^{1}H NMR spectra of organometallic compounds to elucidate the nature of the ligand–metal bond and to illuminate the potential of these compounds for interaction with biological active systems [1, 2]. Although ^{13}C NMR spectroscopy has been employed in only a few cases in the past, it is now receiving a rapid growing interest as an effective tool for investigation of organometallic complexes [3–5]. Recent advances in NMR instrumentation have made it possible to record spectra for many nuclei in the periodic table including those having low relative receptivity such as ^{29}Si, ^{195}Pt, ^{199}Hg ... etc.

Transition metal complexes of weak donor ligands have an obvious interest for being useful starting materials in organometallic synthesis [6]. Recently, organomercury complexes have received increasing attention in view of the increasing evolution of the heavy metal hazards which runs parallel to worldwide industrialization [7]. Mercury, released to the environment as the metal or as compounds such as alkylmercury pesticides or fungicides, has been shown to constitute a serious health hazard. The development of nondestructive techniques to analyse for the presence of mercury would be highly fruitful. Therefore, ^{199}Hg NMR appears to be a logical useful technique for this problem.

Results and Discussion

In previous reports we discussed the synthesis and characterization of some *N*-alkylimines derived from 2-acetylthiophenes, 2-substituted acetophenones and other similar compounds [8, 9]. The stereochemistry of the free imines was established by ^{1}H and ^{13}C NMR spectroscopy. The NMR data showed that these imines exist in solution at ambient temperature as an equilibrating E/Z-diastereoisomeric mixture for some compounds and in a single E-diastereoisomer for others [8, 9].

In the present study we report the reduction of some *N*-alkylimines to the corresponding secondary amines (Scheme 1, **1a–13a**) as well as the synthesis and characterization of amine complexes with mercuric chloride (Scheme 1, **1b–13b**).

$R^1–CH(R^2)–NHR^3$ $HgCl_2L_2$

	R_1	R_2	R_3		L
1a	Ph	H	n-butyl	**1b**	**1a**
2a	2-$NO_2C_6H_4$	H	n-butyl	**2b**	**2a**
3a	1-naphthyl	H	n-butyl	**3b**	**3a**
4a	Ph	H	t-butyl	**4b**	**4a**
5a	1-naphthyl	H	t-butyl	**5b**	**5a**
6a	1-naphthyl	CH_3	t-butyl	**6b**	**6a**
7a	2-thienyl	4-$CH_3C_6H_4$	CH_3	**7b**	**7a**
8a	2-thienyl	4-$CH_3C_6H_4$	isopropyl	**8b**	**8a**
9a	2-thienyl	4-ClC_6H_4	isopropyl	**9b**	**9a**
10a	2-thienyl	4-$NO_2C_6H_4$	isopropyl	**10b**	**10a**
11a	2-thienyl	4-$CH_3C_6H_4$	t-butyl	**11b**	**11a**
12a	2-thienyl	4-ClC_6H_4	t-butyl	**12b**	**12a**
13a	2-thienyl	4-$NO_2C_6H_4$	t-butyl	**13b**	**13a**

Scheme 1.

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TABLE 1. ^{1}H NMR Data of the Free Amines in $CDCl_3$ at 28 °C[a] $R^1-CH(R^2)-NH-R^3$

No.	R^1	R^2	R^3	δ(CH)	δ(R^1)	δ(R^2)	δ(N–R^3)	δ(NH)[b]
	$CH_3-(CH_2)_3-NH_2$*						0.91; 0.97; 1.43; 2.68 [0.88]; [1.35]; [1.42]; [2.56]	1.40 [1.49]
	$(CH_3)_3C-NH_2$*						1.14 [1.06]	1.31 [1.44]
	$(CH_3)_2NH$*						2.51 [2.45]	4.50 [4.56]
1a	Ph	H	n-butyl	3.78	7.32	3.78	0.90; 0.96; 1.44; 2.63	2.35
2a	2-NO_2–Ph	H	n-butyl	4.02	7.26–7.57	4.02	0.91; 0.96; 1.44; 2.63	2.40
3a	1-naphthyl	H	n-butyl	4.18	7.35–8.04	4.18	0.91; 0.96; 1.44; 2.64	2.32
4a	Ph	H	t-but	3.72	7.30	3.72	1.17	2.43
5a	1-naphthyl	H	t-but	4.80	7.21–8.13	4.80	1.22	2.45
6a	1-naphthyl	CH_3	t-but	4.92	7.20–8.11	2.45	1.37	3.05
7a	2-thienyl	4-$CH_3C_6H_4$	CH_3	4.87	6.78[c]; 6.96[d]; 6.82[e]	2.30[g]; 7.20[f]	2.38	3.50
8a	2-thienyl	4-$CH_3C_6H_4$	$CH(CH_3)_2$	5.13	6.74[c]; 6.86[d]; 6.98[f]	2.29[g]; 7.59[f]	1.10; 3.42	3.65
9a	2-thienyl	4-ClC_6H_4	$CH(CH_3)_2$	4.86	6.85[c]; 6.97[d]; 7.12[e]	7.50[f]	1.25; 4.22	3.72
10a	2-thienyl	4-$NO_2C_6H_4$	$CH(CH_3)_2$	5.23	6.76[c]; 6.97[d]; 7.28[e]	8.08[f]	1.28; 4.32	3.80
11a	2-thienyl	4-$CH_3C_6H_4$	t-but	5.19	6.57[c]; 6.84[d]; 6.93[e]	2.35; 7.54[f]	1.25	3.83
12a	2-thienyl	4-ClC_6H_4	t-but	5.22	6.66[c]; 7.03[d]; 7.10[e]	7.63[f]	1.15	3.87
13a	2-thienyl	4-$NO_2C_6H_4$	t-but	5.24	6.70[c]; 7.08[d]; 7.18[e]	7.51[f]	1.49	3.91

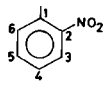
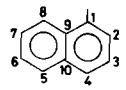
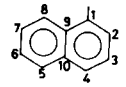
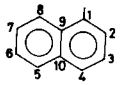
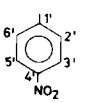
[a] δ value in ppm relative to TMS, data in square parentheses represent chemical shifts in DMSO-d_6 and the open data are in $CDCl_3$. Starred item is parent amine. [b] Broad peak. [c] Signal of H_3 of the thienyl ring. [d] Signal of H_4 of the thienyl ring. [e] Signal of H_3 of the thienyl ring. [f] Midpoint of the AB system of the XC_6H_4 ring. [g] Signal of 4-CH_3.

TABLE II. ^{1}H NMR Data of the Amine-Mercuric Chloride Complexes in DMSO-d_6 at 28 °C[a]

No.	R^1	R^2	R^3	δ(CH)	δ(R^1)	δ(R^2)	δ(R^3)	δ(NH)[b]
	$[CH_3(CH_2)_3-NH_2]_2HgCl_2$						0.93; 0.98; 1.42; 2.65	1.50
	$[(CH_3)_3CNH_2]_2HgCl_2$						1.15	1.35
	$[(CH_3)_2NH]_2HgCl_2$						1.10	4.50
1b	Ph	H	n-butyl	4.00	7.40	4.00	0.85; 0.92; 1.40; 2.50	3.35
2b	2-$NO_2C_6H_4$	H	n-butyl	4.03	7.54–8.03	4.03	0.84; 0.91; 1.38; 2.63	3.36
3b	1-naphthyl	H	n-butyl	4.46	7.50–7.96	4.46	0.85; 0.91; 1.43; 2.86	3.35
4b	Ph	H	t-butyl	3.88	7.27–7.42	3.88	1.22	3.53
5b	1-naphthyl	H	t-butyl	4.27	7.37–8.10	4.27	1.28	3.39
6b	1-naphthyl	CH_3	t-butyl	5.32	7.50–8.31	5.50	1.32	3.40
7b	2-thienyl	4-$CH_3C_6H_4$	CH_3	5.11	7.21[e]; 6.93[f]; 7.21[g]	2.28[c]; 7.13[d]	2.33	3.51
8b	2-thienyl	4-$CH_3C_6H_4$	$CH(CH_3)_2$	4.95	7.23[e]; 6.95[f]; 7.23[g]	2.29[c]; 7.86[d]	1.15; 4.12	3.42
9b	2-thienyl	4-ClC_6H_4	$CH(CH_3)_2$	4.92	7.26[e]; 6.97[f]; 7.26[g]	8.39[d]	1.18; 4.13	3.39
10b	2-thienyl	4-$NO_2C_6H_4$	$CH(CH_3)_2$	5.30	7.28[e]; 6.98[f]; 7.28[g]	7.88[d]	1.16; 4.08	3.40
11b	2-thienyl	4-$CH_3C_6H_5$	t-but	5.32	7.22[e]; 6.94[f]; 7.22[g]	2.27[c]; 7.58[d]	1.08	3.34
12b	2-thienyl	4-ClC_6H_4	t-but	5.25	7.23[e]; 6.95[f]; 7.23[g]	7.57[d]	1.37	3.35
13b	2-thienyl	4-$NO_2C_6H_4$	t-but	5.35	7.27[e]; 6.96[f]; 7.27[g]	8.23[d]	1.39	3.34

[a] δ value relative to TMS. [b] Broad signal. [c] Signal of 4-CH_3 attached to the ring. [d] AB system of the 4-XC_6H_4 measured at midpoint. [e] H_3 signal of the thienyl group. [f] H_4 signal of the thienyl group. [g] H_5 signal of the thienyl group.

TABLE III. ^{13}C NMR Spectra of $HgCl_2L_2$ in DMSO-d_6 at 28 °C[a]

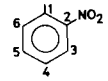
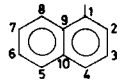
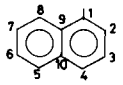
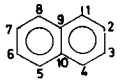
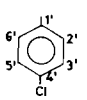
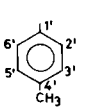
No.	R^1	R^2	R^3	δ(CH)	δ(C-1)	δ(C-2)	δ(C-3)	δ(C-4)
	$[CH_3(CH_2)_3-NH_2]_2HgCl_2$ $[(CH_3)_3CNH_2]_2HgCl_2$ $[(CH_3)_2NH]_2HgCl_2$							
1b		H	n-butyl	52.90 (130.6)	138.28 (159.9)	122.13 (160.7)	128.80 (161.6)	127.30 (160.6)
2b		H	n-butyl	49.08 (130.8)	148.82 (–)	133.62 (–)	133.27 (–)	128.57 (165.5)
3b		H	n-butyl	49.11 (129.8)	136.10 (–)	128.58 (158.6)	127.45 (158.8)	127.60 (158.5)
4b		H	t-butyl	53.77 (130.1)	138.32 (–)	122.11 (160.0)	128.87 (160.6)	127.28 (160.4)
5b		H	t-but	49.80 (130.3)	138.50 (–)	128.20 (159.6)	127.05 (159.5)	126.80 (159.6)
6b		CH_3	t-but	50.20 (139.0)	142.78 (–)	127.52 (160.1)	126.75 (160.5)	125.52 (160.1)
7b			CH_3	58.70 (137.4)		147.19 (–)	130.91 (171.3)	128.95 (171.4)
8b			$CH(CH_3)_2$	56.54 (–)		146.70 (–)	128.22 (170.2)	127.05 (170.2)
9b			$CH(CH_3)_2$	56.60 (–)		146.68 (–)	128.23 (170.5)	127.15 (171.8)
10b			$CH(CH_3)_2$	57.63 (136.6)		146.85 (–)	128.26 (171.5)	127.21 (171.5)
11b			t-but	52.70		146.95 (–)	128.06 (170.1)	127.10 (170.1)
12b			t-but	56.50 (136.7)		150.80 (–)	128.92 (170.3)	127.65 (170.2)
13b			t-but	56.20 (138.2)		150.34 (–)	129.39 (170.6)	127.36 (170.7)

[a] δ value in ppm relative to TMS. [b] Assignment for C-7 to C-10. [c] Signal of 4-CH_3. [d] Signal of C-1' of the 4-XC_6H_4.

δ(C-5)	δ(C-6)	δ (others)[b]	δ(R^2)	δ(R^3)
				14.10; 20.21; 36.48; 42.15 32.65; 47.50 39.52
128.80 (160.7)	122.13 (159.9)			13.86; 20.12 (125.0) (125.0) 31.67; 49.50 (125.0) (131.0)
131.33 (160.6)	124.34 (164.5)			13.68; 19.67; 30.88 (125.0) (125.0) (125.0) 49.96 (131.2)
125.87 (158.4)	125.36 (158.6)	125.10; 123.53; 131.4; 133.21 (158.6) (158.4) (–) (–)		13.56; 19.66; 29.36 (125.0) (125.0) (125.0) 48.32 (131)
128.87 (160.6)	122.11 (160.2)			28.00; 49.36 (–) (125.0)
125.11 (159.4)	125.40 (159.6)	124.95; 123.54; 128.55; 133.18 (158.9) (159.4) (–) (–)		29.05; 47.15 (–) (125.0)
125.34 (160.5)	125.17 (160.4)	123.35; 121.94; 127.75; 133.09 (160.3) (160.4) (–) (–)	25.05 (129.0)	28.96; 46.85 (–) (125.0)
127.30 (172.5)			22.85[c]; 148.87[d]; 138.93[e] (125.0) (–) (–) 129.00[f]; 127.05[g] (160.0) (158.2)	20.61 (133.0)
127.81 (171.5)			22.78[c]; 148.03[d]; 137.20[e] (176.0) (–) (–) 129.41[f]; 127.32[g] (160.0) (153.2)	22.31; 46.10 (133.0) (125.0)
127.75 (171.8)			149.60[d]; 138.39[e]; 128.98[f] (–) (–) (164.0) 128.04[g] (149.3)	22.19; 45.82 (133.0) (125.1)
127.90 (172.7)			149.65[d]; 147.92[e]; 138.70[f] (–) (–) (164.3) 127.80[g] (159.5)	22.08; 45.27 (133.3) (125.2)
127.60 (171.2)			22.63[c]; 147.60[d]; 138.39[e] (126.0) (–) (–) 128.98[f]; 128.20[g] (159.3) (164.0)	28.86; 52.43 (133.0) (125.0)
128.70 (170.7)			148.70[d]; 137.20[e]; 128.85[f] (–) (–) (164.0) 128.51[g] (159.2)	29.82; 51.86 (125.0) (–)
128.90 (171.3)			148.86[d]; 137.28[e]; 128.63[f] (–) (–) (162.2) 128.54[g] (159.4)	28.78; 52.46 (125.2) (–)

[e]Signal of C-4′ of the 4-XC_6H_4. [f]Signal of C-3′ and C-5′ of the 4-XC_6H_4. [g]Signal of C-2′ and C-6′ of the 4-XC_6H_4.
[h]Data between parenthesis represent $^1J(^{13}C-H)$.

TABLE IV. ^{13}C NMR Chemical Shifts of the Free Amines in $CDCl_3$ at 28 °C[a]

No.	R^1	R^2	R^3	δ(CH)	δ(C-1)	δ(C-2)	δ(C-3)	δ(C-4)
	$CH_3(CH_2)_3NH_2$ $(CH_3)_3CNH_2$ $(CH_3)_2NH$							
1a		H	n-butyl	54.41 (130.0)	140.44 (–)	122.04 (160.0)	122.28 (160.8)	122.04 (161.2)
2a		H	n-butyl	50.84 (131.2)	149.24 (–)	135.79 (–)	133.13 (167.3)	127.81 (165.4)
3a		H	n-butyl	51.63 (130.0)	136.15 (–)	128.69 (158.7)	127.54 (158.6)	127.55 (159.1)
4a		H	t-but	50.67 (130.2)	141.49 (–)	128.34 (160.1)	128.16 (160.7)	127.34 (161.3)
5a		H	t-but	50.78 (130.2)	136.85 (–)	128.58 (159.7)	127.46 (159.9)	126.17 (159.8)
6a		CH_3	t-butyl	50.20 (138.7)	141.31 (–)	122.69 (160.2)	127.63 (160.6)	125.81 (160.4)
7a			CH_3	59.70 (137.3)		150.12 (–)	129.70 (171.2)	126.85 (171.2)
8a			$CH(CH_3)_2$	59.71 (136.0)		150.12 (–)	129.65 (170.3)	126.88 (170.3)
9a			$CH(CH_3)_2$	59.18 (137.4)		149.93 (–)	129.85 (170.5)	127.12 (170.5)
10a			CH	59.25 (138.5)		149.35 (–)	129.86 (171.6)	127.22 (171.6)
11a			t-but	56.89 (136.4)		150.64 (–)	129.05 (170.1)	127.11 (170.1)
12a			t-but	56.53 (136.8)		150.67 (–)	128.92 (170.2)	127.70 (170.2)
13a			t-but	56.47 (138.2)		150.21 (–)	129.37 (170.6)	127.28 (170.6)

[a]δ value in ppm relative to TMS; open data represent chemical shifts in $CDCl_3$ and those in square parentheses are in DMSO-d_6. [b]Assignment for C-7 to C-10 respectively. [c]Ligand of 4-CH_3. [d]δ value of C-1′ of the 4-XC_6H_4.

δ(C-5)	δ(C-6)	δ (others)[b]	δ(R^2)	δ(R^3)
				13.97; 20.08; 36.11; 42.04 [14.13] [20.22] [36.40] [42.05] 32.55; 47.32 [32.60] [47.02] 39.45 [39.51]
122.28 (160.8)	126.81 (160.0)			13.97; 20.42; 32.17 (126.0) (126.0) (126.0) 48.20 (133.0)
131.21 (166.5)	124.64 (164.6)			13.97; 20.43; 32.17 (126.0) (126.0) (126.0) 49.31 (133.2)
125.98 (158.8)	125.40 (159.4)	125.22; 123.52; 133.86; 131.80 (159.3) (159.2) (–) (–)		13.98; 20.52; 32.26 (125.8) (125.8) (125.8) 49.73 (132.9)
126.87 (160.7)	126.63 (160.1)			29.18; 47.20 (125) (–)
125.88 (159.7)	125.40 (159.7)	124.70; 123.78; 133.86; 131.92 (159.2) (159.1) (–) (–)		29.06; 44.68 (125) (–)
125.34 (160.2)	123.76 (160.2)	123.06; 121.94; 130.16; 133.63 (159.7) (159.6) (–) (–)	24.26 (128.0)	24.95; 46.82 (125) (–)
127.43 (172.5)			22.72[c]; 147.91[d]; 136.67[e] (132.0) (–) (–) 128.31[f]; 126.99[g] (159.2) (160.2)	23.84 (133.0)
127.72 (171.4)			21.04[c]; 148.90[d]; 138.67[e] (132.0))–) (–) 129.04[f]; 126.93[g] (159.2) (160.3)	23.24; 45.97 (126.3) (134.0)
128.83 (171.7)			148.85[d]; 137.25[e]; 129.15[f] (–) (–) (159.2) 126.98[g] (164.0)	22.78; 48.04 (126.3) (134.0)
128.72 (172.8)			149.26[d]; 146.38[e]; 139.01[f] (–) (–) (164.2) 126.92[g] (159.3)	29.92; 51.87 (125.1) (–)
128.47 (171.3)			22.70; 149.26[d]; 146.38[e]; 139.01[f] (131.8) (–) (–) (164.2) 126.92 (159.6)	29.92; 51.87 (125.1)
128.60 (170.8)			148.78[d]; 137.14[e]; 128.60[f] (–) (–) (159.2) 128.42[g] (164.1)	29.74; 51.75 (125.2) (–)
128.86 (171.2)			148.50[d]; 137.63[e]; 129.20[f] (–) (–) (164.0) 126.88[g] (159.2)	28.77; 52.31 (125.3) (–)

[e] Signal of C-4′ of the 4-XC_6H_4. [f] Signal of C-3′ and C-5′ of the 4-XC_6H_4. [g] Signal of C-2′ and C-6′ of the 4-XC_6H_4.
[h] Data in parentheses represent $^1J(^{13}C-H)$.

The amine–mercuric chloride complexes have been investigated on the bases of their ^{1}H, ^{13}C, ^{199}Hg NMR data, which are reported for the first time as well, as their elemental analysis.

It is well documented in the literature that most compounds containing the C=N group are reducible under suitable conditions [10]. The C=N group is generally more easily reducible than the corresponding carbonyl group. The reduction process depends on the pH value of the solution in that the protonated and tautomeric forms may be the reduced species [10]. Protonation will occur in order to establish the equilibrium (eqn. (1)). The electronegativity

$$R^1\text{–}\underset{\displaystyle R^2}{\overset{|}{C}}\text{=N=}YR^3 \xrightarrow{H^+} [R^1\text{–}\underset{\displaystyle R^2}{\overset{|}{C}}\text{=N–}YR^3]H^+ \xrightarrow{2e + 2H^+}$$

$$R^1\text{–}\underset{\displaystyle R^2}{\overset{|}{C}}\text{=}N^+H_2 + HYR^3 \xrightarrow{2e + H^+} R^1\text{–}\underset{\displaystyle R^2}{\overset{|}{C^+}}HNH_3 \qquad (1)$$

of the Y atom in different compounds containing the C=N group (e.g. imines, nitrones, oxaziridines..., etc.) plays an effective role in the reduction process [10].

Aldimines and ketimines are reducible in a wide pH range, but as they are usually easily hydrolyzed both in acid and alkaline solution, they are difficult to investigate. Both classical and controlled potential reductions are reported to yield the expected secondary amine; many of the classical reductions were performed in 50% sulphuric acid at 0 °C. In some cases, it is advantageous to work in a non-aqueous medium [10].

In this study the reduction process has been carried out using $NaBH_4$, which is one of the complex metal hydrides having moderate reduction power towards imines and has the great advantage of being unstable in hydroxylic solvents [11]. The results indicate that reduction of imines by this method lead to high yields (85–96%).

^{1}H NMR Spectra

The ^{1}H NMR chemical shifts of the free amines were recorded in chloroform-d at ambient temperature and are presented in Table I. The solvent effect should be taken into account when comparing shieldings of the free amines with their mercuric chloride complexes shifts since the amine–mercuric chloride complexes are not soluble in chloroform-d. The ^{1}H NMR spectrum of compound **1a** shows in chloroform-d signals at δ 3.78 for CH; δ 7.32 for phenyl protons; δ 2.35 for NH and δ 0.90, 0.96, 1.44, 2.63 for the n-butyl protons. The ^{1}H NMR results (Table I) indicate that the reduction process has been successfully achieved and the data are in a good fit for the suggested structures, Scheme 1. General observation on the data (Table I) indicate that the NH signal was broad and the position was variable too. The 4-substituted aryl groups of the compounds **7a–13a** exhibit the well known AB system.

The reaction of amines with metal chlorides has received few reports in literature and was found to follow eqn. (2) on an equimolar basis of the reactants [7, 12].

$$HgCl_2 + 2L \longrightarrow HgCl_2L_2 \qquad (2)$$

where L = amine ligands

The ^{1}H NMR of amine–mercuric chloride complexes, Table II, in dimethylsulphoxide-d_6 revealed the presence of an NH signal and incorporation of the solvent (methanol) in the formation of these complexes was not observed [13, 14]. The above observations have also been confirmed by ^{13}C NMR data (Table III) and were also found to agree with the element analysis. The ^{1}H NMR data for these complexes (Table II) show that compound **1b**, for example, has signals at δ 0.85, 0.92, 1.40, 2.50 for n-butyl protons; δ 3.35 for NH; δ 4.00 for CH and δ 7.40 for phenyl protons. It is obvious when comparing these figures with those for the free amine ligand **1a**, that the different in shielding is negligible taking into account the solvent effect. Other ^{1}H NMR data for these complexes are in general similar to the ^{1}H NMR data of the parent amine ligands.

^{13}C NMR Spectra

The ^{13}C NMR chemical shifts, Table IV, are known to be sensitive to both electronic and steric effects which makes a detailed interpretation of the data require an understanding of the influence of the various substituents. Indeed, it has been suggested that an inductive/field effect influences distant carbon chemical shifts [2, 4]. Assignment of these resonances was relatively straightforward since the effect of the substituents on the shieldings could be approximately predicted from the known effects of the same analogues of monosubstituted benzene, using the assumption of additivity of substituent chemical shift effect (SCS).

The ^{13}C NMR chemical shifts, Table IV were obtained from proton decoupled spectra and the interpretation has been achieved on the bases of the ^{1}H NMR spectra as well as $^{1}J(^{13}C\text{–}H)$ coupling constants (Table IV) obtained from NOE spectra. For the free amines the range of the ^{13}C chemical shifts for the CH group, resulting from reduction of the C=N, were δ 50.20–59.71; the *N*-alkyl carbons were δ 13.97–49.73; δ 24.95–52.31 and δ 23.24–44.68 for *N*-n-butyl, *N*-t-butyl and *N*-isopropyl respectively. The ^{13}C NMR spectra clearly show the normal order of the aromatic signal *viz.* $\delta_{ipso} > \delta$ of other carbons (Table IV).

The $^1J(^{13}C-H)$ coupling constants can be approximated empirically with the knowledge of the s character in sp, sp^2 and sp^3 of the carbon hybrid orbital. Accordingly, the values have been predicted to be 125, 165 and 250 Hz [15].

The ^{13}C NMR chemical shifts and the coupling constants for the amine–mercuric chloride complexes in the present study (Table III) remained almost unchanged compared with the data of the parent molecules (free amines), Table IV, taking into account the solvent effect. For example, compound **1b** showed that aromatic carbons resonated in the range δ 122.13–138.28 and the *N*-alkyl carbons were at δ 13.86–49.56 whereas ranges for the free amine (**1a**) were at δ 122.04–140.44 and δ 13.93–48.20 for the aromatic and *N*-alkyl carbons respectively. Further evidence comes from $^1J(^{13}C-H)$ coupling constants where both the free amines (Table IV) and the complexes (Table III) show the same magnitude. Furthermore, $^2J(^{13}C-H)$ coupling constants of these complexes were found to be in the range 3.66–4.90 and 4.27–5.53 Hz for the *N*-alkyl and the aromatic $^{13}C-H$ coupling respectively.

The dependence of the ^{13}C shieldings in these amine–mercuric chloride complexes appears explicable in terms of a weak dative bond between the nitrogen and the mercury atoms [4, 7]. In the case of a strong metal–ligand bond, the ^{13}C chemical shifts would exhibit considerable downfield shift. Evidence for this suggestion comes from the ^{13}C NMR spectra of four-coordinate platinum–imine complexes. The δ value of these complexes showed downfield shift of *ca.* 12.4 and 6.8 ppm for the *N*-alkyl and *C*-alkyl attached to the C=N group respectively when compared with the parent free imine [3]. Further evidence from a previous study, indicates that the ^{13}C resonances of some alkynylgold and alkynylsilver complexes suffer considerable downfield shifts ranging from 20–36 ppm for C_α and from 8–14 for C_β upon coordination to the metal, compared with the parent alkynes [4].

The ^{13}C NMR data available in the literature for organometallic compounds indicate that numerous trends have been noted in ^{13}C chemical shifts [2, 4]. Several attempts have been made to correlate the ^{13}C parameters with other constants [2, 4]. The literature data suggest that the polarizability of the metal make changes in the charge distribution of the metal in the $^{13}C-M-X$ fragment causing major changes in the shieldings of the ^{13}C shifts [1, 2, 7].

The ^{13}C NMR chemical shifts in the present study indicate that the shieldings of the $^{13}C-N-M$ signal remain unchanged compared with the free amines. Recently, similar behaviour has been reported for some mercuric chloride, $SbCl_3$ and $BiCl_2$ complexes where the NMR chemical shifts shieldings were rationalized in terms of a weak degree of polarizability of the $^{13}C-N-M$ bonds [4, 7]. There is also clear evidence in the literature based on NMR spectroscopic data utilizing isotope labelling indicating that this sort of coordination is well demonstrated in the case of alkyl substituted ureas [16]. Accordingly, it is believed that coordination of amines with mercuric chloride occur utilizing the nitrogen lone pair of electrons. Investigation of the electronic configuration of $HgCl_2$ indicates that dative bonds can be formed between the metal and the nitrogen lone pair of electrons to form the corresponding complexes where sp hybridization is available [12, 13].

^{199}Hg NMR Spectra

The first direct observation of ^{199}Hg NMR was reported in 1959 by Dessy *et al.* [17]. Later ^{199}Hg FT NMR studies have indicated that this technique can be a potentially useful tool to investigate several mercury containing compounds such as pesticides, fungicides and other related compounds where concentrations as low as 10^{-2} M are practicable. All alkyl mercury compounds were found to exhibit ^{199}Hg resonances more shielded than that of dimethylmercury [1]. Other workers presented results for inorganic mercury salts; they found that these compounds were also more shielded than dimethyl mercury [18]. Moreover, ^{199}Hg chemical shifts of a series of aromatic mercury compounds have also been found to exhibit upfield shift larger than dimethylmercury. Accordingly, dimethylmercury has been recommended as an internal reference at δ 0.0 for measuring ^{199}Hg chemical shifts. The organometallic compounds containing mercury cover on extremely large chemical shift range, *ca.* 3000 ppm [1, 2].

The ^{199}Hg chemical shifts of the present study are listed in Table V and were found to lie in the range *ca.* −1200 to −1496 ppm relative to dimethylmercury. An important feature of the ^{199}Hg NMR signals of all the studied compounds was that the signals were very broad and the linewidth at $\frac{1}{2}w$ was in the range 24–53 Hz. This behaviour has not been observed for $HgCl_2$, $Hg(CH_3)_2$ and other C–Hg signals where in all these cases, the signal was very sharp. The broadening of the ^{199}Hg NMR signals is good support for N–Hg bonding since coupling between nitrogen and mercury atoms could be responsible for this broadening.

The $N-^{199}Hg$ coupling constants are expected to be less than 15 Hz as a result of a weak dative bond between the nitrogen and mercury atoms. Directly bonded $^{13}C-^{199}Hg$ coupling constants were found to be in the range 1186 to 3196 Hz; two bonded coupling constants were in the range 72 to 126 Hz for some phenyl mercury compounds [2]. The coupling constants between nitrogen and ^{199}Hg of these complexes was confirmed when dimethylamine labelled by nitrogen-15 was reacted with $HgCl_2$ to achieve the corresponding complex. Recording ^{199}Hg NMR spectrum showed that the ^{199}Hg signal appeared

TABLE V. ^{199}Hg NMR Data of the Mercury Chloride Complexes in DMSO-d_6 at 28 °C[a,b]

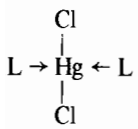
No.	R^1	R^2	R^3	δ(N–^{199}Hg)	Linewidth (Hz)
	$[(CH_3(CH_2)_3NH_2]_2HgCl_2$*			–1242.3	39
	$[(CH_3)_3CNH_2]_2HgCl_2$*			–1252.4	39
	$[(CH_3)_2NH]_2HgCl_2$*			–1301.4	39
1b	Ph	H	n-butyl	–1340.9	42
2b	2-$NO_2C_6H_4$	H	n-butyl	–1368.8	42
3b	1-$C_{10}H_2$	H	n-butyl	–1358.2	48
4b	Ph	H	t-but	–1338.8	53
5b	1-naphthyl	H	t-but	–1393.0	53
6b	1-naphthyl	CH_3	t-but	–1392.0	52
7b	2-thienyl	4-$CH_3C_6H_4$	CH_3	–1316.9	24
8b	2-thienyl	4-$CH_3C_6H_4$	$CH(CH_3)_2$	–1452.0	24
9b	2-thienyl	4-ClC_6H_4	$CH(CH_3)_2$	–1465.0	24
10b	2-thienyl	4-$NO_2C_6H_4$	$CH(CH_3)_2$	–1496.0	24
11b	2-thienyl	4-$CH_3C_6H_4$	t-but	–1200.2	24
12b	2-thienyl	4-ClC_6H_4	t-but	–1224	24
13b	2-thienyl	4-NO_2	t-but	–1495	24

[a] δ value relative to dimethylmercury signal at 0.0 ppm. Starred item is parent amine complex. [b] $^{199}HgCl_2$ signal appeared at 1501.6 under the same conditions. [c] For labelling see Scheme 1.

at –1298 ppm as a doublet due to coupling with nitrogen-15. The magnitude of this coupling was found to be 14.7 Hz which gives good support for the above results.

Further support for this view comes from platinum–imine complexes which indicate that the nitrogen fairly coordinated to the mercury compared with the nitrogen coordinated to platinum. In most imine complexes, the range of $^1J(^{195}Pt–N^{14})$ was 271–288 Hz [19]. These values are comparable to the values of $^1J(^{195}Pt–N^{14})$ obtained from analogous square planar platinum complexes (292–304 Hz). Assuming no isotope effect, ^{15}N coupling should be larger than ^{14}N coupling by the ratio of their gyromagnetic constants (a factor of 1.4). The observed value for $^1J(^{195}Pt–N^{14})$ of 283 Hz is in agreement with the observed and calculated value of $^1J(^{195}Pt–N^{15})$ of analogous compounds [19]. Broad resonances due to the N^{14} splitting are not fully resolved, due to N^{14} relaxation [19]. These observations confirm once again the results obtained from ^1H and ^{13}C NMR data in which a weak bond was demonstrated between the mercury and the nitrogen atom.

Accordingly, the following four-coordinate structure (**II**) is suggested for these amine–mercuric chloride complexes which is in good agreement with some analogous mercury complexes [7].



II

Experimental

All the imines were prepared following standard methods and their ^1H and ^{13}C NMR spectra have been reported in previous work [8, 9, 20].

Reduction Procedure

The imines were converted to the corresponding amines by taking the relevant prepared imine solution (30 mmol) in absolute MeOH (20 ml) in a two-necked round-bottomed flask equipped with magnetic stirrer, condenser and thermometer. The flask was inserted in an ice bath to cool it to –10 °C. To this $NaBH_4$ (35 mmol) was added while stirring the solution. The stirring continued for an additional two hours. Then the temperature of the flask was raised to room temperature at first and then increased to 50 °C for another two hours. Then the solution was cooled to room temperature and the solvent was removed. Distilled water (30 ml) was added and the whole lot was transferred to a separating funnel, where the compound was extracted with 150 ml diethyl ether. The separated ethereal layer was further washed with water. Finally the obtained ethereal layer was dried over Na_2SO_4 overnight. Then the solvent was removed and the crude material was distilled under vaccum to obtain the product [11].

The microanalytical data and the physical properties are as follows:

1a (boiling point (b.p.) 86 °C/1.0 Torr) yield 89%. *Anal.* Calc. for $C_{11}H_{17}N$: C, 80.93; H, 10.49; N, 8.50. Found: C, 80.65; H, 10.32; N, 8.25%.

2a (b.p. 131–133 °C/0.9 Torr) yield 90.0%. *Anal.* Calc. for $C_{11}H_{16}H_2O_2$: C, 63.45; H, 7.74; N, 13.45; O, 15.36. Found: C, 63.15; H, 7.62; N, 13.23%.

3a (b.p. 150–157 °C/1.7 Torr) yield 87%. *Anal.* Calc. for $C_{15}H_{19}N$: C, 84.46; H, 8.97; N, 6.57. Found: C, 84.33; H, 8.75; N, 6.26%.

4a (b.p. 65–67 °C/2.0 Torr) yield 94%. *Anal.* Calc. for $C_{11}H_{17}N$: C, 80.93; H, 10.49; N, 8.58. Found: C, 80.81; H, 10.32; N, 8.26%.

5a (b.p. 104–105 °C/0.1 Torr) yield 86%. *Anal.* Calc. for $C_{15}H_{19}N$: C, 84.46; H, 8.97; N, 6.57. Found: C, 84.25; H, 8.96; N, 6.36%.

6a (b.p. 122–125 °C/0.3 Torr) yield 92%. *Anal.* Calc. for $C_{16}H_{21}N$: C, 84.54; H, 9.30; N, 6.16. Found: C, 84.35; H, 9.10; N, 5.90%.

7a (b.p. 112–115 °C/0.5 Torr) yield 85%. *Anal.* Calc. for $C_{13}H_{15}NS$: C, 71.83; H, 6.98; N, 6.44. Found: C, 71.62; H, 6.76; N, 6.25%.

8a (b.p. 105–108 °C/0.2 Torr) yield 86%. *Anal.* Calc. for $C_{15}H_{19}NS$: C, 73.43; H, 7.80; N, 5.71. Found: C, 73.15; H, 7.61; N, 5.52%.

9a melting point (m.p.) 127–128 °C, crystallized from methanol, yield 94%. *Anal.* Calc. for $C_{14}H_{16}N_2O_2S$: C, 60.85; H, 5.83; N, 10.14; O, 11.58. Found: C, 60.64; H, 5.62; N, 9.80%.

10a m.p. 133–134 °C, crystallized from methanol, yield 85%. *Anal.* Calc. for $C_{14}H_{16}ClNS$: C, 63.27; H, 6.10; Cl; 13.34; S, 12.02; N, 5.27. Found: C, 63.00; H, 5.95; Cl, 13.15; N, 4.85%.

11a (b.p. 122–125 °C/0.3 Torr) yield 89%. *Anal.* Calc. for $C_{16}H_{21}NS$: C, 74.09; H, 8.15; S, 12.36; N, 5.40. Found: C, 73.85; H, 8.00; N, 5.15%.

12a m.p. 158–159 °C, crystallized from methanol, yield 95%. *Anal.* Calc. for $C_{15}H_{18}N_2O_2S$: C, 61.96; H, 6.23; N, 9.63; S, 11.07; O, 11.01. Found: C, 61.82; H, 6.00; N, 9.70%.

13a m.p. 167–168 °C, crystallized from methanol, yield 93%. *Anal.* Calc. for $C_{15}H_{18}ClNS$: C, 64.41; H, 6.48; Cl, 12.67; S, 11.43; N, 5.01. Found: C, 64.23; H, 6.35; Cl, 12.50; N, 4.80%.

Preparation of Mercuric Chloride Complexes

All the reactions for the preparation of the mercuric chloride complexes were carried out under a nitrogen atmosphere in a three-necked flask equipped with magnetic stirrer, condenser and N_2 inlet. To a hot solution of amine (0.01 mol) in methanol (25 ml) a solution of $HgCl_2$ (0.01 mol) in methanol (20 ml) was added dropwise over a period of 30 min. The reaction mixtures were then refluxed for 3 h with stirring, giving the corresponding amine–mercuric chloride complexes [7].

The microanalytical data and physical properties are as follows:

1b m.p. 130–131 °C, crystallized from methanol, yield 95%. *Anal.* Calc. for $C_{22}H_{34}N_2HgCl_2$: C, 44.19; H, 5.73; N, 4.68; Hg, 33.54; Cl, 11.86. Found: C, 44.00; H, 5.52; N, 4.45; Cl, 11.60%.

2b m.p. 128–129 °C, crystallized from methanol, yield 92%. *Anal.* Calc. for $C_{22}H_{32}N_4O_4HgCl_2$: C, 38.41; H, 4.68; N, 8.14; O, 9.30; Hg, 29.16; Cl, 10.31. Found: C, 38.25; H, 4.48; N, 7.96; Cl, 10.15%.

3b m.p. 114–115 °C, crystallized from methanol, yield 96%. *Anal.* Calc. for $C_{30}H_{38}N_2HgCl_2$: C, 51.62; H, 5.48; N, 4.01; Hg, 28.73; Cl, 10.16. Found: C, 51.35; H, 5.36; N, 3.94; Cl, 10.05%.

4b m.p. 123–124 °C, crystallized from methanol, yield 95%. *Anal.* Calc. for $C_{22}H_{34}N_2HgCl_2$: C, 44.19; H, 5.73; N, 4.68; Hg, 33.54; Cl, 11.86. Found: C, 44.00; H, 5.48; N, 4.56; Cl, 11.72%.

5b m.p. 155–156 °C, crystallized from methanol, yield 96%. *Anal.* Calc. for $C_{30}H_{38}N_2HgCl_2$: C, 51.62; H, 5.48; N, 4.01; Hg, 28.73, Cl, 10.16. Found: C, 51.47; H, 5.26; N, 3.82; Cl, 10.10%.

6b m.p. 150–152 °C, crystallized from methanol, yield 96%. *Anal.* Calc. for $C_{32}H_{42}N_2HgCl_2$: C, 52.93; H, 5.82; N, 3.86; Hg, 27.62; Cl, 9.65. Found: C, 52.71; H, 5.60; N, 3.72; Cl, 9.65%.

7b m.p. 120–122 °C, crystallized from methanol, yield 93%. *Anal.* Calc. for $C_{26}H_{30}N_2S_2HgCl_2$: C, 44.22; H, 4.29; N, 3.97; S, 9.08; Hg, 28.40; Cl, 10.04. Found: C, 44.00; H, 4.10; N, 3.76; Cl, 9.85%.

8b m.p. 126–128 °C, crystallized from methanol, yield 95%. *Anal.* Calc. for $C_{32}H_{34}N_2S_2HgCl_2$: C, 49.14; H, 4.38; N, 3.58; S, 8.20; Hg, 25.64; Cl, 9.06. Found: C, 48.90; H, 4.22; N, 3.46; Cl, 8.95%.

9b m.p. 122–124 °C, crystallized from methanol, yield 96%. *Anal.* Calc. for $C_{28}H_{32}N_4O_4S_2HgCl_2$: C, 40.80; H, 3.91; N, 6.80; O, 7.76; S, 16.39; Hg, 24.34; Cl, 8.60. Found: C, 40.61; H, 3.82; N, 6.63; Cl, 8.45%.

10b m.p. 108–110 °C, crystallized from methanol, yield 96%. *Anal.* Calc. for $C_{28}H_{32}N_2S_2HgCl_4$: C, 41.88; H, 4.01; N, 3.49; S, 7.08; Hg, 24.98; Cl, 17.66. Found: C, 41.68; H, 3.90; N, 3.10; Cl, 17.50%.

11b m.p. 130–131 °C, crystallized from methanol, yield 94%. *Anal.* Calc. for $C_{32}H_{42}N_2S_2HgCl_2$: C, 48.63; H, 5.35; N, 3.54; S, 8.13; Hg, 25.38; Cl, 8.97. Found: C, 48.42; H, 5.10; N, 3.32; Cl, 8.88%.

12b m.p. 127–128 °C, crystallized from methanol, yield 95%. *Anal.* Calc. for $C_{30}H_{36}N_4O_4S_2HgCl_2$: C, 42.28; H, 4.25; N, 6.57; O, 7.51, S, 7.53; Hg, 23.54; Cl, 8.32. Found: C, 42.11; H, 4.08; N, 6.35; Cl, 8.20%.

13b m.p. 140–142 °C, crystallized from methanol, yield 95%. *Anal.* Calc. for $C_{30}H_{36}N_2S_2HgCl_4$: C, 43.35; H, 4.36; N, 3.37; S, 7.73; Hg, 24.13; Cl, 17.06. Found: C, 43.20; H, 4.26; N, 3.15; Cl, 16.95%.

NMR Spectra

The NMR spectra were obtained on a Jeol JNM FX-100 spectrometer operating in the Fourier Transform (FT) mode. All the spectra were recorded at ambient temperature 28 °C and the sample concentration was generally 0.3 M in the appropriate

solvent. Chemical shifts were determined relative to the internal standard tetramethylsilane (TMS) for ^{1}H and ^{13}C spectra and relative to $(CH_3)_2Hg$ for ^{199}Hg spectra.

(i) ^{1}H NMR spectra

^{1}H observed frequency 100 MHz; pulse width 20 μs (45°); pulse delay auto set, acquisition time auto set, data points 8k; spectral width 1000 Hz; effective resolution 0.10 Hz, probe temperature 28 °C, sample tubes 10 mm, probe $^{1}H/^{13}C$ dual probe and deuterium internal lock.

(ii) ^{13}C NMR spectra

^{13}C observed frequency 25 MHz; pulse width 10 μs (45°); pulse delay 15 s, acquisition time auto set; data points 8k; spectral width 5000 Hz, effective resolution 0.15 ppm, sample tube 10 mm; probe $^{1}H/^{13}C$ dual probe, ^{1}H noise decoupling and internal lock on the deuterium signal of the solvent.

(iii) ^{199}Hg NMR spectra

^{199}Hg observe frequency 17.75 MHz; pulse width 15 μs (45°); pulse delay 2 s; acquisition time auto set; data points 8k; spectral width 10 000 Hz; sample tube 10 mm; probe multi-probe; ^{1}H noise decoupling and internal lock on deuterium signal of the solvent.

Chemical shifts [1] were computed with respect to $(CH_3)_2Hg$ (neat) at 0.0 ppm and checked against $HgCl_2$ (1 M) in DMSO-d_6 at −1501.6 ppm.

(iv) Nuclear Overhauser Enhancement (NOE) measurements [21]

The absolute NOE determined at 25 MHz was recorded after gating the decoupler to allow interrupted (pulse modulated) ^{1}H decoupling. Using the technique of decoupling just before the short ^{13}C pulses and during short (1 μs) acquisition of the free-induction decays, while leaving the decoupler off for the longer ($\leqslant 4T_1$) pulse intervals, allowed direct measurements of NOE values from the ^{1}H decoupled spectra.

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