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*NOTE*

# Adducts of Bismuth(III) Nitrate with Some Lewis Bases

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Solutions of $Bi(NO_3)_3 \cdot 5H_2O$ in dimethyl formamide react with some Lewis bases to form 1 : 1, 1 : 2 or 2 : 1 adducts. The Lewis bases used were pyridine, bipyridyl, *o*-phenanthroline, aniline, *o* , *m*-, *p*-toluidines, triethylamine, formamide, acetamide, benzamide, acetanilide, urea, thiourea, dimethylsulphoxide, naphthalene, anthracene and phenanthrene. The Lewis base molecules coordinate with the bismuth atom.

Bismuth nitrate pentahydrate is extremely hygroscopic and it is difficult to handle it in atmospheric conditions. The solution of this salt in DMF precipitates out adducts easily with O-, N-, S- donor Lewis bases. These adducts are quite stable and can be handled easily in atmospheric conditions. Some adducts of bismuth salts with arenes and other compounds have been reported[1], but not with naphthalene, anthracene and phenanthrene.

All the chemicals used were of AR grade. The reactions were carried out in dry conditions. 1 g bismuth nitrate was dissolved in 20 mL DMF and the required amount of the Lewis base was slowly added to the solution with shaking. The adducts precipitate out either in cold or just by slight warming. Bismuth nitrate and arene hydrocarbon were boiled in chloroform for about 6 h and on cooling crystals of the adducts separated out. The adduct complexes were filtered and washed three to four times with dry petroleum ether and dried.

Bismuth was estimated gravimetrically as BiOI. Nitrogen, sulphur, carbon and hydrogen were estimated by standard methods using semimicro methods. Molecular weights of the complexes were determined by Rast's method. Magnetic susceptibilities were measured at room temperature by Gouy's method. IR spectra of the compounds were recorded on Perkin-Elmer IR-621.

All the adducts are either white or light-coloured solids and stable in dry atmosphere. They decompose before melting giving volatile products leaving behind oligomeric products. The analytical data are in agreement with the stoichiometry of the complexes. Molecular weight measurements indicate their monomeric nature. The magnetic moment values ($\mu_{eff}$ *ca.* 0.33 B.M.) indicate the diamagnetic nature of all the complexes.

The modes of bonding of the ligands have been suggested on the basis of IR spectra of the complexes. Upon complex formation, the pyridine (1 : 1 adduct) vibrations in the high frequency region are not shifted appreciably but there is a shift noted in the low frequency region. The in-plane ring deformations and out-of-plane ring deformations are shifted to higher frequencies at 640 and 470 $cm^{-1}$ respectively; ν(Bi—N) appeared at 350 $cm^{-1}$ suggesting coordination of pyridine to bismuth through N atom.[2] The high frequency region bands in the *o*-phenanthroline

(1 : 1 adduct) and bipyridyl adduct (1 : 1 adduct) are not metal sensitive. The $\nu$(Bi—N) appeared at *ca.* 375 $cm^{-1}$, indicating their coordination through N atom.[3]

TABLE-1

ANALYTICAL DATA OF ADDUCTS OF BISMUTH TRINITRATE

| Formula of the adduct | Colour | Elemental analysis (%) Found (Calcd) | | |
|---|---|---|---|---|
| | | Bi | C | N |
| $Bi(NO_3)_3\cdot C_5H_5N$ | White | 44.81 | 12.32 | 11.49 |
| (Pyridine) | | (44.09) | (12.65) | (11.81) |
| $Bi(NO_3)_3\cdot C_{12}H_8N_2$ | Pink | 36.53 | 25.41 | 12.03 |
| (*o*-Phenanthroline) | | (36.34) | (25.04) | (12.17) |
| $Bi(NO_3)_3\cdot C_{10}H_8N_2$ | Dark green | 37.69 | 21.87 | 12.58 |
| (2,2′-Bipyridyl) | | (37.93) | (21.77) | (12.70) |
| $Bi(NO_3)_2\cdot 2C_6H_5NH_2$ | White | 35.36 | 24.43 | 12.27 |
| (Aniline) | | (35.97) | (24.78) | (12.04) |
| $Bi(NO_3)_3\cdot 2C_7H_7NH_2$ | Brown | 34.25 | 27.70 | 11.63 |
| (*o*-Toluidine) | | (34.31) | (27.58) | (11.49) |
| $Bi(NO_3)_3\cdot 2C_7H_7NH_2$ | Brownish | 34.03 | 27.89 | 11.29 |
| (*m*-Toluidine) | | (34.31) | (27.58) | (11.49) |
| $Bi(NO_3)_3\cdot 2C_7H_7NH_2$ | Dark brown | 34.18 | 27.78 | 11.63 |
| (*p*-Toluidine) | | (34.31) | (27.58) | (11.49) |
| $Bi(NO_3)_3\cdot 2HCONH_2$ | White | 43.44 | — | 14.63 |
| (Formamide) | | (43.09) | (4.94) | (14.43) |
| $Bi(NO_3)_3\cdot CH_3CONH_2$ | Dirty white | 46.50 | — | 12.51 |
| (Acetamide) | | (45.03) | (5.28) | (12.33) |
| $Bi(NO_3)_3\cdot 2C_6H_5CONH_2$ | White | 33.18 | 26.52 | 11.21 |
| (Benzamide) | | (32.81) | (26.37) | (10.98) |
| $Bi(NO_3)_3\cdot 2C_6H_5NHCOCH_3$ | Dirty yellow | 31.25 | 28.61 | 10.71 |
| (Acetanilide) | | (31.42) | (28.87) | (10.52) |
| $Bi(NO_3)_3\cdot 2NH_2CONH_2$ | White | 40.87 | — | 10.73 |
| (Urea) | | (40.58) | (4.66) | (10.87) |
| $Bi(NO_3)_3\cdot 2NH_2CSNH_2$ | Yellow | 37.18 | — | 17.61 |
| (Thiourea) | | (37.79) | (4.38) | (17.91) |
| $Bi(NO_3)_3\cdot 2(CH_3)_2SO$ | White | 38.00 | 8.92 | 7.73 |
| (Dimethyl sulphoxide) | | (37.93) | (8.71) | (7.62) |
| $Bi(NO_3)_3\cdot 2N(C_2H_5)_3$ | White | 35.32 | 24.32 | 11.91 |
| (Triethylamine) | | (35.00) | (24.12) | (11.72) |
| $2Bi(NO_3)_3\cdot C_{10}H_8$ | Yellow | 45.12 | 12.92 | 9.31 |
| (Naphthalene) | | (45.53) | (13.07) | (9.15) |
| $2Bi(NO_3)_3\cdot C_{14}H_{10}$ | Brown | 43.43 | 17.51 | 8.83 |
| (Anthracene) | | (43.18) | (17.35) | (8.67) |
| $2Bi(NO_3)_3\cdot C_{14}H_{10}$ | Dirty brown | 42.93 | 17.21 | 8.81 |
| (Phenanthrene) | | (43.18) | (17.35) | (8.67) |

The IR spectra of the aniline (1 : 2 adduct), *o*-, *m*- and *p*-toluidine adducts showed $\nu_{asym}$(NH) at *ca.* 3425 $cm^{-1}$, $\nu_{sym}$(N—H) at *ca.* 3375 $cm^{-1}$ and $\delta$(N—H) at *ca.* 1600 $cm^{-1}$. The $\nu$(C—N) appeared at *ca.* 1320 $cm^{-1}$ and 1210 $cm^{-1}$ somewhat lowered due to N—Bi bonding in the adduct.[4] The band at *ca.* 350 $cm^{-1}$ may be assigned to $\nu$(Bi—N) indicating coordination of the ligands through N-atom to bismuth.

The IR spectra of the formamide (1 : 2 adduct), acetamide (1 :1 adduct), benzamide (1 : 2 adduct), acetanilide (1 : 2 adduct) urea (1 : 2 adduct) and thiourea (1 : 2 adduct) showed bands at *ca.* 3420, 3310 and 3200 $cm^{-1}$ which may be assigned to $\nu_{asym}$(NH) and $\nu_{sym}$(NH). The lowering of the ν(C=O) band at *ca.* 1425 $cm^{-1}$ as compared to the free ligands indicated that the amides are coordinated to the bismuth atom through oxygen atom.[5] The ν(Bi—O) in these adducts appeared at *ca.* 330 $cm^{-1}$ as two or three bands. The lowering of ν(C=S) from 1086 $cm^{-1}$ to 990 $cm^{-1}$ in the thiourea adduct (1 : 2 adduct) indicates that thiourea molecule is attached to bismuth atom through S-atom.[8] The ν(Bi—S) band is assigned at *ca.* 300 $cm^{-1}$.[7]

The IR spectra of DMSO adduct (1 : 2 adduct) showed ν(S=O) at 970 $cm^{-1}$ which is lower than that in free DMSO, indicating that it is bonded through oxygen to bismuth.[8] The ν(Bi—O) may be assigned at *ca.* 325 $cm^{-1}$.

In the IR spectra of naphthalene, phenanthrene and anthracene adducts (2 : 1 adduct) the split in ν(C—H) points out the difference in the various hydrogen atoms in the aromatic hydrocarbon molecules. The decrease in C—C skeletal vibrations and appearance of new lines in the region *ca.* 1600, 1450 and 1375 $cm^{-1}$ may be attributed to the fact that these adducts are formed by means of the π-electrons. The IR spectra point out that the interaction between bismuth and hydrocarbon molecule is strong enough to produce considerable π-electron localization. The lone pair on bismuth is ideally suited for backbonding to the π-system. Thus the hydrocarbon molecules behave as a π-allene like complexing agent.[11]

All the adducts showed peaks at *ca.* 1400 and *ca.* 1250 $cm^{-1}$ which may be assigned to $\nu_{asym}$(O—N—O) and $\nu_{sym}$(O—N—O) while bands at *ca.* 825 $cm^{-1}$ may be due to ν(N—O) [12]. The existence of more than one band in the region *ca.* 320 $cm^{-1}$ indicates the nitrate group joined through oxygen atom to the bismuth. There are no bands in the region *ca.* 3400 $cm^{-1}$ indicating the absence of water of crystallisation.

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