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COORDINATION COMPOUNDS OF BISMUTH. BISMUTH(III) DERIVATIVES OF DI(*o*-AMINOPHENYL)DISULFIDE AND DI(*p*-TOLYL)DISULFIDE

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ABSTRACT

Bismuth metal reacts with di(*o*-aminophenyl)disulfide ($(o\text{-}H_2NC_6H_4S)_2$ and di(*p*-tolyl)disulfide ($(p\text{-}MeC_6H_4S)_2$ in refluxing toluene to give the compounds $Bi(SC_6H_4NH_2\text{-}o)_3$ and $Bi(SC_6H_4Me\text{-}p)_3$ in high yield. The reaction of bismuth with a mixture of iodine and $(o\text{-}H_2NC_6H_4S)_2$ or $(p\text{-}Me\text{-}C_6H_4S)_2$ gives the compounds $BiI(SC_6H_4NH_2\text{-}o)_2$, $BiI(SC_6H_4Me\text{-}p)_2$, $BiI_2(SC_6H_4NH_2\text{-}o)$ and $BiI_2(SC_6H_4Me\text{-}p)_2$. Adducts of some of the above compounds with 1,10-phenanthroline and 2,2'-bipyridyl were also prepared. The compounds and adducts were characterised by microanalyses, infrared, UV/Visible spectroscopy and conductivity measurements.

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INTRODUCTION

Complexes of both main group and transition metals with sulphur donor ligands are of much current interest[1-5] . The electrochemical oxidation of a metal in a non-aqueos solution of disulfide is a convenient and direct route to neutral thiolato complexes of elements such as zinc, cadmium, mercury[6], tin, lead[7], indium and thallium[2]. The direct reaction between indium or tin metal with $(C_6H_5)_2E_2$ (E = S, Se) to give the neutral comounds $In(EC_6H_5)_3$ or $Sn(EC_6H_5)_4$ has been used recently by Tuck et al.[8]

The crystal structure of bismuth tris(diethylphosphorodithioate), $[Bi(C_2H_5)_2PS_2)_3]$, has been determined by Iglesias et al.[9]

In this paper the oxidative addition of the -S-S- linkage of di(*o*-aminophenyl)disulfide and di(*p*-tolyl)disulfide to bismuth metal, reactions of these disulfides with different molar ratios of iodine and bismuth metal are discussed. Also reported is the preparation of some bismuth compound adducts with the neutral donor bases, 1,10-phenanthroline (phen) and 2,2' bipyridyl (bipy).

EXPERIMENTAL

General Data

Bismuth metal (Fluka) was available in the form of 0.6 cm diameter rods. Toluene and the substituted thiols were used as supplied (Fluka). The disulfides were synthesised by standard methods[10].

C, H, N microanalyses were carried out using a Carlo Erba Analyzer type 1106. Infrared spectra were recorded on a Perkin-Elmer 580 infrared spectrophotometer using CsI pellets, UV/visible spectra were recorded on a Shimadzu UV/Visible recording spectrophotometer UV/160. Conductance measurements were carried out at room temperature in DMF solution (10^{-3} M) using a Jenway 4070 conductivity meter.

Syntheses

$Bi(SC_6H_4NH_2\text{-}o)_3$ and $Bi(SC_6H_4Me\text{-}p)_3$. A mixture of finely cut bismuth metal (0.21 g, 1 mmol) and the disulfide (1.5 mmol) in toluene (50 mL) was refluxed for 3 h. The unreacted bismuth (0.1 g) was removed by filtration, and the resultant orange or black solutions were reduced to ca. 1/3 of their volume. The resulting solids were then collected by filtration, washed with petroleum ether (b. p. 60-80) and dried in vacuo, yield, 0.53 g and 0.50 g, respectively.

$BiI(SC_6H_4NH_2\text{-}o)_2$ and $BiI(SC_6H_4Me\text{-}p)_2$. Finelly cut bismuth metal (0.21 g, 1 mmol) was refluxed with (0.25 g, 1 mmol) $(SC_6H_4NH_2\text{-}o)_2$ or (0.24 g, 1 mmol) $(SC_6H_4Me\text{-}p)_2$ and iodine (0.065 g, 0.5 mmol) in toluene (30 mL). A dark brown or black solution, respectively, was formed after 4 h reflux, after which time the unreacted bismuth metal (0.03 g) was filtered off, the solid obtained after the volume of the solution was reduced to ca. 1/3, was washed with petroleum ether (b.p. 60-80) and dried in vacuo, yield, 0.52 g and 0.5 g, respectively.

$BiI_2(SC_6H_4NH_2\text{-}o)$ and $BiI_2(SC_6H_4Me\text{-}p)$. These were prepared in a similar way except that (0.13 g, 1 mmol) iodine was used along with the disulfide (0.5 mmol), yield 0.52 g and 0.40 g, respectively.

$Bi(SC_6H_4NH_2\text{-}o)_3$.bipy. $Bi(SC_6H_4NH_2\text{-}o)_3$ (0.59 g, 1 mmol) was stirred with 2,2`-bipyridine (0.16 g, 1 mmol) in benzene (30 mL) for 2 h during which time a red oil was formed. The colourless solution was decanted and the oil was triturated with diethyl ether (30 mL). The resultant maroon solid was dried in vacuo, yield 0.7 g.

$Bi(SC_6H_4NH_2\text{-}o)_3.phen$. Reaction of $Bi(SC_6H_4NH_2\text{-}o)_3$ (0.58 g, 1 mmol) and 1,10-phenanthroline (0.18 g, 1 mmol) in methanol (10 mL) yielded an orange oil, which became a solid after stirring for 2 h at room temperature. This solid was collected, washed with methanol (3x5 mL), and dried in vacuo, yield 0.72 g.

The analog derivatives $Bi(SC_6H_4Me\text{-}p)_3$.bipy and $Bi(SC_6H_4Me\text{-}p)_3$.phen were prepared similarly, yield 0.68 g and 0.7 g respectively.

RESULTS AND DISCUSSION

The method described represents a simple and efficient one-pot synthesis of a number of $Bi(SC_6H_4NH_2\text{-}o)_3$ or $Bi(SC_6H_4Me\text{-}p)_3$ compounds by direct reactions (oxidative addition). These reactions are noticeably simpler than those used in the past for the preparation of $M(SPh)_n$ compounds of main group elements involving metathetical reaction[1,11,12] of MCl_n with Na(SPh), Li(SPh) or $Mg(SPh)_2$.

The most likely primary reaction is that shown in equation (1) giving a +1 oxidation state species. In the case of bismuth, indium and tin this would be followed by the reaction of equation (2), (M = Bi, In, n = 3, M = Sn, n = 4).

$$2M + (RS)_2 \longrightarrow 2M(RS) \qquad (1)$$

$$2M(RS) + (n\text{-}1)(RS)_2 \longrightarrow 2M(RS)_n \qquad (2)$$

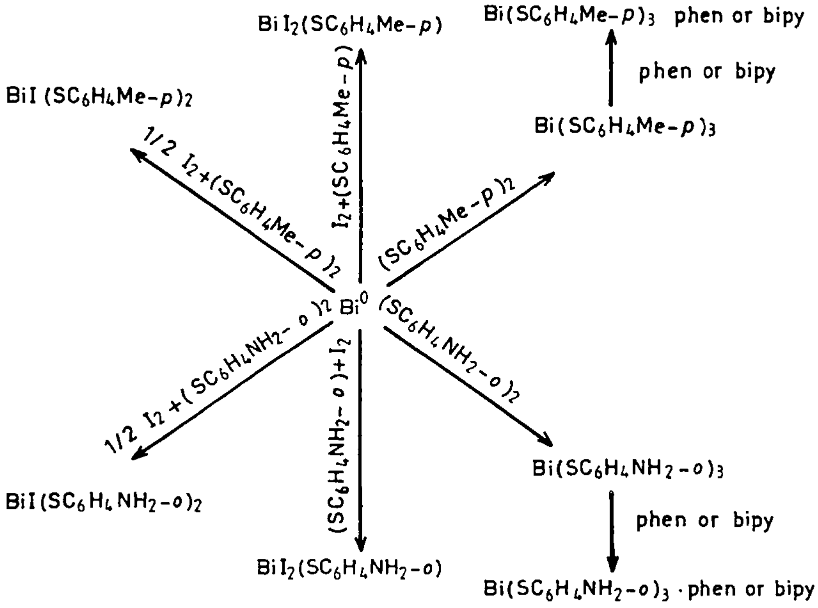

Fig. 1. Scheme of the Reactions of Bi^{o}

The oxidative insertion process of equation (2) is clearly analogous to known reactions involving the conversions[13] $In^0 \longrightarrow In^{3+}$ or $Sn^{2+} \longrightarrow Sn^{4+}$.

The formation of the compounds $Bi(SC_6H_4NH_2\text{-}o)_3$ and $Bi(SC_6H_4Me\text{-}p)_3$, their oxidation and their reactions are summarized in Fig. 1.

The compounds and adducts were isolated as coloured solids. Their melting points, elemental analyses and conductivities are listed in Table I. The most important diagonistic features of the IR spectra are listed in Table II. The IR bands of the free ligands $(SC_6H_4NH_2\text{-}o)_2$ are shown for comparison. Medium absorption bands are observed in the 3389-

Table I. Analytical Data of the Compounds and Adducts

Compound	Empirical formula	Formula weight	Colour	Yield (%)	Melting point (°C)	C%	Analysis^a H%	N%	Λ_{mol} Ω^{-1} cm^2 mol^{-1}
$Bi(SC_6H_4NH_2\text{-}o)_3$	$C_{18}H_{18}N_3S_3Bi$	581.16	Orange	91	148	37.15 (37.10)	3.09 (2.99)	7.22 (7.02)	8.1
$BiI(SC_6H_4NH_2\text{-}o)_2$	$C_{12}H_{12}S_2N_2IBi$	679.00	Brown	90	118	24.65 (24.45)	2.06 (2.01)	4.79 (4.80)	31.2
$BiI_2(SC_6H_4NH_2\text{-}o)$	$C_6H_6SNI_2Bi$	598.84	Brown	87	220	12.26 (12.20)	1.02 (1.00)	2.38 (2.40)	55
$Bi(SC_6H_4NH_2\text{-}o)_3$.bipy	$C_{28}H_{28}S_3N_5Bi$	739.16	Maroon	92	154	45.56 (45.51)	3.52 (3.39)	9.49 (9.50)	28.9
$Bi(SC_6H_4NH_2\text{-}o)_3$.phen	$C_{30}H_{26}S_3N_5Bi$	761.16	Dark Orange	95	180	46.18 (46.10)	3.59 (3.61)	8.98 (9.03)	24.7
$Bi(SC_6H_4Me\text{-}p)_3$	$C_{21}H_{21}S_3Bi$	578.16	Black	89	338 (d)	43.55 (45.50)	3.63 (3.68)	-	9.2
$BiI(SC_6H_4Me\text{-}p)_2$	$C_{14}H_{14}S_2IBi$	582.00	Black	89	335 (d)	28.85 (28.82)	2.40 (2.60)	-	23.7
$BiI_2(SC_6H_4Me\text{-}p)$	$C_7H_7SI_2Bi$	586.00	Black	87	>360	14.33 (14.20)	1.19 (1.21)	-	33.8
$Bi(SC_6H_4Me\text{-}p)_3$.bipy	$C_{31}H_{29}S_3N_2Bi$	734.16	Dark yellow	92	>360	49.01 (50.11)	4.08 (4.01)	3.94 (3.95)	15.1
$Bi(SC_6H_4Me\text{-}p)_3$.phen	$C_{33}H_{29}S_3N_2Bi$	758.16	Orange	92	298	52.24 (52.11)	3.83 (3.80)	3.69 (3.71)	18.9

a = Calculated values in parentheses. d = decomposition

Table II. IR Absorption (cm^{-1}) and Electronic Data for the Free Ligands and Compounds

Compound	IR				UV/Visible		
	ν(C-S)	$\nu(NH_2)$	ν(Bi-S)	ν(Bi-N)	Band maxima λ (nm) ε ($dm^3\ mol^{-1}\ cm^{-1}$)		
$(SC_6H_4NH_2\text{-}o)_2$	1040 (s)	3395 (s)	-	-	284(12150)	348(23400)	-
$Bi(SC_6H_4NH_2\text{-}o)_3$	1065 (s)	3255 (s)	325 (w)	437 (m)	267(13630)	346(19050)	388(24780)
$BiI(SC_6H_4NH_2\text{-}o)_2$	1080 (m)	3260 (s)	320 (m)	420 (m)	273(16350)	350(19950)	376(24790)
$BiI_2(SC_6H_4NH_2\text{-}o)$	1070 (s)	3265 (s)	329 (m)	440 (m)	280(14710)	-	378(23540)
$Bi(SC_6H_4NH_2\text{-}o)_3$.bipy	1060 (s)	3390 (s)	330 (w)	270 (w)	278(24950)	355(18510)	384(34380)
$Bi(SC_6H_4NH_2\text{-}o)_3$.phen	1075 (m)	3395 (s)	330 (w)	250 (w)	288(24930)	-	388(21560)
$(SC_6H_4Me\text{-}p)_2$	1000 (s)	-	-	-	247(6500)	398(23930)	-
$Bi(SC_6H_4Me\text{-}p)_3$	1030 (m)	-	350 (m)	-	264(16500)	359(19410)	390(24790)
$BiI(SC_6H_4Me\text{-}p)_2$	1025 (m)	-	340 (w)	-	250(17500)	399(21280)	-
$BiI_2(SC_6H_4Me\text{-}p)$	1020 (s)	-	330 (w)	-	251(19800)	-	387(24790)
$Bi(SC_6H_4Me\text{-}p)_3$.bipy	1030(s)	-	335 (w)	250 (m)	266(24730)	-	371(19820)
$Bi(SC_6H_4Me\text{-}p)_3$.phen	1025 (m)	-	330 (m)	270 (m)	244(21420)	-	381(17850)

s = strong, m = medium, w = week

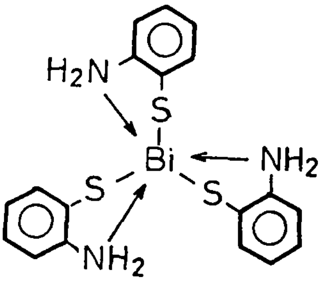

Fig. 2. Suggested Structure of $Bi(SC_6H_4NH_2\text{-}o)_3$

3395 cm^{-1} region and are assigned to $\nu(NH_2)$. The derivative compounds give medium bands in the region 3255-3265 cm^{-1} indicating that the NH_2 group is involved in the coordination to the metal[14]. The $\nu(C\text{-}S)$ band is observed at 1000-1040 cm^{-1} for the free ligands and upon coordination these values are increased (Table II). Further support for this coordination was provided by the appearance of new bands at about 320-355 and 420-470 cm^{-1} which are tentively attributed[14,15] to $\nu(Bi\text{-}S)$ and $\nu(Bi\text{-}N)$, respectively. It may be concluded that there is an octahedral geometry around the bismuth atom in the case of the $SC_6H_4NH_2\text{-}o$ ligand as shown in Fig. 2. Hexa-coordinated compounds of bismuth[9] and indium were described elsewhere[19].

Furthermore, the IR spectra of the adducts show a medium band around 3390 cm^{-1} which is assigned to uncoordinated $\nu(NH_2)$ while the $\nu(C\text{-}S)$ band is observed at 1065 cm^{-1} indicating that the ligands are coordinated through sulfur. Further support for this was obtained from the appearance of new bands at 320-355 cm^{-1} which are assigned to $\nu(Bi\text{-}S)$, while the $\nu(Bi\text{-}N)$ absorption of the phenanthroline and bipyridine adducts are in good agreement with the reported values for $InX_3.1.5$ phen (X = Cl, Br, I) which fall in the range[17] 270-220 cm^{-1}.

The UV/Visible spectra of the compounds are similar to one another but different from those of the ligands (Table II). The broad band observed in the range 245-350 nm is due to π-π^* transitions of the free ligands, while a new additional band was observed for all compounds and adducts in the range 355-390 nm. This band can be attributed to the charge transfer transition from the filled ligand orbitals to the vacant metal orbitals.

The molar conductivities of 10^{-3} M solutions of the compounds and adducts indicate that these compounds and adducts are non-electrolytes[18] in DMF.

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