

## Ring Opening in a Non-basic Medium of 2-Methyl-6-nitrobenzothiazole and H-D Exchange at the 2-Methyl promoted by Silver(I)

By **Michele Aresta**,\* Istituto di Chimica Generale ed Inorganica, Università, Via Amendola 173,70126 Bari, Italy  
**Francesco Ciminale**, Istituto di Chimica Organica, Università, Via Amendola 173,70126 Bari, Italy

Silver(I) promotes H-D exchange at the 2-methyl group of 2-methyl-6-nitrobenzothiazole (mnbt) in the presence of CD<sub>3</sub>OD in dimethyl sulphoxide (dmsO). Moreover, the alcohol in dmsO causes nucleophilic attack at the C<sup>2</sup> of mnbt with subsequent cleavage of the C-S bond and opening of the thiazole ring to afford (2-amino-5-nitrobenzenethiolato-S)silver(I). In a similar reaction, the unsubstituted benzothiazole ring is opened to afford the silver(I) salt of 2-aminobenzenethiol. The role of the electronic structure of silver(I) in the ring-opening reaction is discussed and compared with the behaviour of analogous complexes of iron(II) and rhodium(I) with MeOH.

RECENTLY we reported that silver(I) promotes the ring-opening reaction of 6-nitrobenzothiazole in a non-basic medium in the presence of alcohols.<sup>1</sup> As an extension of our studies on the properties of metal complexes with benzothiazole derivatives<sup>1,2</sup> and with a view to investigating the role of both the electronic structure of the metal and the effect of the substituents on the benzothiazole ring on the behaviour of the co-ordinated ligand, we have prepared complexes of silver(I), iron(II), and rhodium(I) with 2-methyl-6-nitrobenzothiazole (mnbt), 6-nitrobenzothiazole (nbt), and benzothiazole (bt) and studied the interaction of the complexes with deuteriated methanol in dimethyl sulphoxide (dmsO).

### RESULTS AND DISCUSSION

*Preparation and Characterization of the Complexes.*—The reaction of Ag[ClO<sub>4</sub>] with mnbt in toluene at room temperature affords [Ag(mnbt)<sub>2</sub>][ClO<sub>4</sub>], a white crystalline compound. Its i.r. spectrum in Nujol mull presents two intense bands at 1110 and 1065 cm<sup>-1</sup>, two medium bands at 907 and 885 cm<sup>-1</sup>, and a strong band at 617 cm<sup>-1</sup> attributed to the ClO<sub>4</sub> group. Conductivity measurements on the solution in *NN*-dimethylformamide (dmf) show that the complex behaves as a 1:1 electrolyte (Table). When the complex is crystallized from dmsO,

significant changes in the i.r. spectra in the range 600—1300 cm<sup>-1</sup>, *i.e.* a more distinct separation of the bands around 1100 cm<sup>-1</sup> and the presence of a very strong band located at *ca.* 900 cm<sup>-1</sup> in the spectrum of the perchlorato-complex.<sup>3</sup>

The reaction of Ag[NO<sub>3</sub>] with an excess of mnbt affords only a white complex of formula [Ag(mnbt)(NO<sub>3</sub>)]. The i.r. spectrum of the solid in Nujol mull shows bands at 1290vs, 1025ms, and 730m cm<sup>-1</sup> that can be attributed to a covalently bonded nitrate group.<sup>4</sup> The second ν<sub>2</sub> band expected at *ca.* 1500 cm<sup>-1</sup> and due to the ν<sub>asym</sub>(NO<sub>3</sub>) cannot be unambiguously assigned because of absorptions due to the ligand. The nitrate group is expected to behave as a unidentate ligand and silver(I) to be linearly two-co-ordinated. It is noteworthy that other silver(I) complexes of formula [Ag(bt)][NO<sub>3</sub>] and [Ag(nbt)][NO<sub>3</sub>] are ionic in the solid state.<sup>1</sup> In dmf solution the [Ag(mnbt)(NO<sub>3</sub>)] complex behaves as a ion pair as suggested by the low value of the molar conductivity.

The i.r. spectrum of the solid complex Fe(nbt)<sub>2</sub>Cl<sub>2</sub> in Nujol mull shows far-i.r. bands at 270m, 265ms, and 212s cm<sup>-1</sup>. These figures suggest a polymeric structure with octahedral geometry around six-co-ordinated iron(II). The u.v. and visible spectrum in dmf supports this

Analytical<sup>a</sup> and physical data for the complexes

Complex	M.p. <sup>b</sup> (θ <sub>c</sub> /°C)	Analysis (%)					Λ <sub>M</sub> <sup>c</sup> S cm <sup>2</sup> mol <sup>-1</sup>
		C	H	M <sup>d</sup>	N	Cl	
[Ag(mnbt) <sub>2</sub> ][ClO <sub>4</sub> ]	242	32.2 (32.25)	2.0 (2.05)	18.1 (18.1)	9.40 (9.40)	5.95 (5.95)	79.5
[Ag(mnbt)(NO <sub>3</sub> )]	167	27.6 (27.45)	1.8 (1.75)	30.9 (30.8)	8.0 (8.0)		36.8
[{Fe(nbt) <sub>2</sub> Cl <sub>2</sub> }] <sub>n</sub>	289	34.6 (34.3)	1.7 (1.65)	11.5 (11.45)	11.5 (11.45)	14.6 (14.6)	11.0
[Ag(S-C <sub>6</sub> H <sub>3</sub> (NH <sub>2</sub> )(NO <sub>2</sub> ))·dmsO] (decomp.)	178	26.6 (27.05)	2.8 (3.10)	30.3 (30.4)	7.85 (7.90)		8.0
[Ag(S-C <sub>6</sub> H <sub>4</sub> (NH <sub>2</sub> ))]	275	31.0 (31.05)	2.6 (2.60)	46.8 (46.5)	6.0 (6.05)		6.0

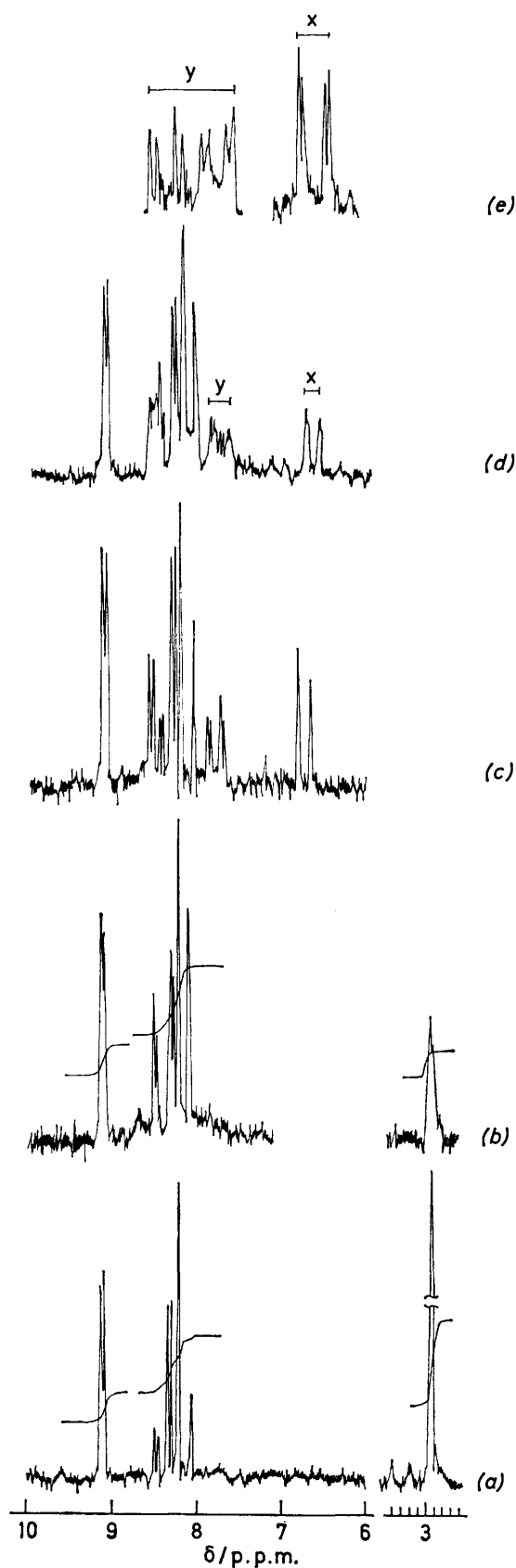
<sup>a</sup> Calculated values are given in parentheses. <sup>b</sup> Uncorrected. <sup>c</sup> For 10<sup>-3</sup> mol dm<sup>-3</sup> solutions in dmf. <sup>d</sup> Silver or iron.

the i.r. spectrum of the solid shows a unique strong band at 1080 cm<sup>-1</sup> and a medium one at 895 cm<sup>-1</sup>, the rest of the spectrum remaining unchanged. The loss of the splitting of the bands at *ca.* 1100 and 900 cm<sup>-1</sup> is best interpreted, in our view, as due to the change of local symmetry of the perchlorate group in the crystal lattice consequent upon recrystallization, rather than to the conversion of a pure covalently bound perchlorato-group to an ionic group. If not, one would expect more

picture as the maxima found at 9060 and 6615 cm<sup>-1</sup> are more characteristic of six-co-ordinate iron(II) than of four-co-ordinate iron(II).<sup>5</sup>

We assume that the ligands are co-ordinated to the metals through the nitrogen atom of the benzothiazole ring, as demonstrated for analogous silver(I) and iron(II) complexes.<sup>1,5</sup>

*Reaction of Silver(I) Complexes with Deuteriomethanol.*—The <sup>1</sup>H n.m.r. spectrum of [Ag(mnbt)<sub>2</sub>][ClO<sub>4</sub>] in [<sup>2</sup>H<sub>6</sub>]-



dmsO presents resonances at  $\delta$  9.10 (1 H, H<sup>7</sup>, d,  $J_{7,5}$  2.5 Hz), 8.37 (1 H, H<sup>5</sup>, dd,  $J_{5,7}$  2.5,  $J_{5,4}$  9.0 Hz), 8.13 (1 H, H<sup>4</sup>, d,  $J_{4,5}$  9.0 Hz), and 2.95 p.p.m. (3 H, 2-CH<sub>3</sub>, s) [Figure (a)]. For the free ligand dissolved in the same solvent these signals are at  $\delta$  9.15, 8.37, 8.13, and 2.90 p.p.m. respectively. These figures show that in the coordinated ligand the 2-CH<sub>3</sub> protons are moderately more acidic than in the free ligand. When CD<sub>3</sub>OD is added to the [2H<sub>6</sub>]dmsO solution of the complex and the sealed n.m.r. tube is heated at *ca.* 40 °C, an H-D exchange at the 2-methyl is evident [Figure (b)]. Once started, H-D exchange proceeds also at room temperature (*ca.* 25 °C). It must be emphasized that the free ligand in the same solvent does not exchange with CD<sub>3</sub>OD even in more drastic conditions (several hours at 90 °C). This reaction gives further evidence for the role of silver(I) in the activation of the 2-position and consequently of the 2-methyl.

After a longer reaction time, when the H-D exchange had proceeded to *ca.* 70%, the n.m.r. spectrum of the silver complex changes to that shown in Figure (c). The new signals at  $\delta$  8.55 (1 H, H<sup>7</sup>, d,  $J_{7,5}$  2.5 Hz), 7.33 (1 H, H<sup>5</sup>, dd,  $J_{5,7}$  2.5,  $J_{5,4}$  8.5 Hz), and 6.63 (1 H, H<sup>4</sup>, d,  $J_{4,5}$  8.5 Hz) p.p.m. are in accordance with the imidatoform (III) in the Scheme. Eventually, a new set of signals appears [Figure (d)] at  $\delta$  8.46 (1 H, H<sup>7</sup>, d,  $J_{7,5}$  2.5 Hz), 7.60 (1 H, H<sup>5</sup>, dd,  $J_{5,7}$  2.5,  $J_{5,4}$  8.5 Hz), 6.61 (1 H, H<sup>4</sup>, d,  $J_{4,5}$  8.5 Hz), and 5.1 (2 H, broad, NH<sub>2</sub>) p.p.m. These signals are assigned to the thiolatosilver complex (IV) and are ill resolved at 60 MHz. At 100 MHz [Figure (e)] the resolution is much better and the multiplicity and coupling constants are well defined. The signals assigned to the open form (IV) are also found in the <sup>1</sup>H n.m.r. spectrum of an authentic sample isolated from the reaction of the silver complex with methanol.

The complex [Ag(mnbt)(NO<sub>3</sub>)] follows a similar path and affords, on opening of the thiazole ring, the compound (IV). The complex [Ag(bt)<sub>2</sub>][NO<sub>3</sub>] gives 2-aminobenzenethiolatosilver(I) identical with an authentic sample obtained from Ag[NO<sub>3</sub>] and 2-aminobenzenethiol.

If one compares the behaviour of the silver(I)-nbt and silver(I)-mnbt complexes towards CD<sub>3</sub>OD, one finds that the former undergo exclusively nucleophilic attack by the alcohol at C<sup>2</sup>, while for the latter, H-D exchange at the 2-methyl is the first observed process.

These different features can be explained as follows. In the case of the nbt ligand, the carbanion resulting from the attack by the alcohol at C<sup>2</sup> is much better stabilized than the ylide<sup>6</sup> formed upon elimination of H<sup>2</sup>, and thus, the ring-opening reaction is the only process observed. However, in the case of the mnbt ligand, both steric and electronic effects of the 2-methyl group render nucleophilic attack by the alcohol less favourable than for nbt. On the other hand, the  $\pi$

<sup>1</sup>H n.m.r. spectra of [Ag(mnbt)<sub>2</sub>][ClO<sub>4</sub>]: (a) in [2H<sub>6</sub>]dmsO; (b) the same sample after addition of CD<sub>3</sub>OD and heating for a few hours at 40 °C; (c) and (d) same sample after a longer time at room temperature; (e) recorded at 100 MHz, 500 Hz sweep width

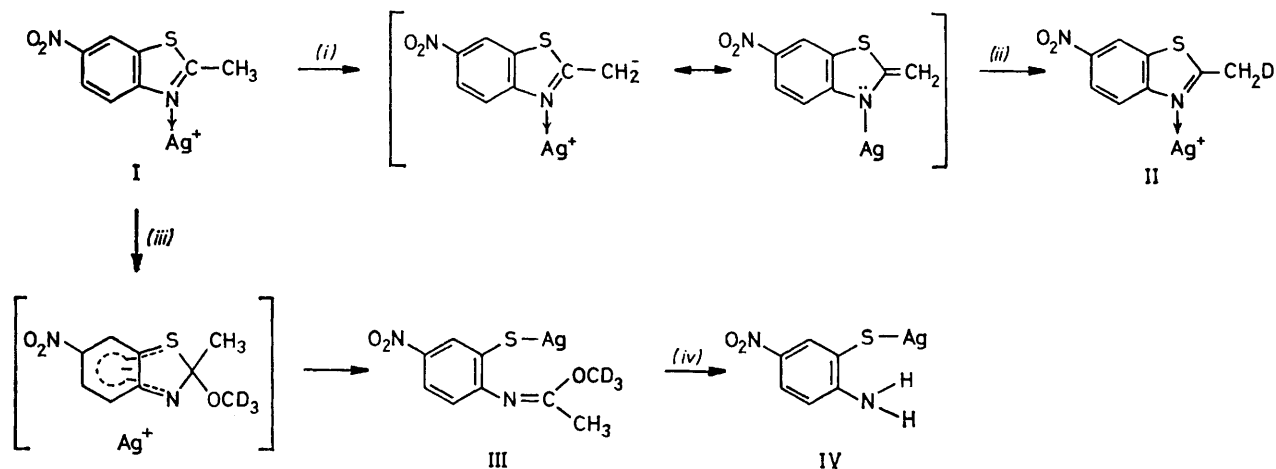
carbanion resulting from proton elimination at the 2-methyl group can be stabilized by resonance (see the Scheme). For these reasons, exchange at the 2-methyl group is the faster process and the ring-opening reaction is slower than for the  $\text{Ag}^{\text{I}}\text{-nbt}$  system.

We have proposed<sup>1</sup> that the closed electronic structure of silver(I), a  $d^{10}$  ion, may be responsible for the benzothiazole reactivity towards alcohols in mild non-basic conditions. It must be emphasized that such ring-opening reactions usually take place in a basic medium<sup>7-10</sup> and in the presence of a transition-metal ion such as  $\text{Pd}^{\text{II}}$  or  $\text{Pt}^{\text{II}}$ .

The slight tendency of silver(I) to expand the co-ordination sphere, especially with hard donor ligands

nbt) are dissolved in dmsO, and methanol added, no nucleophilic attack is observed at  $\text{C}^2$  of the benzothiazole ring, since the ligand is released, as is also shown by the  $^1\text{H}$  n.m.r. spectrum. The system behaves just like the free ligand when added to alcohol, and it is known that no reaction is observed under these conditions, nor at temperatures around  $100^\circ\text{C}$  in the absence of base.

The complex  $[\text{Rh}(\text{bt})(\text{C}_8\text{H}_{12})\text{Cl}]^2$  ( $\text{C}_8\text{H}_{12}$  = cyclo-octa-1,5-diene) in  $\text{CDCl}_3$  treated with  $\text{CD}_3\text{OD}$  has  $^1\text{H}$  n.m.r. signals at  $\delta$  9.20 (1 H,  $\text{H}^2$ , s), 8.87 (1 H,  $\text{H}^7$ , d,  $J_{7,6}$  8.0,  $J_{7,5}$  2.5 Hz), 7.97 (1 H,  $\text{H}^4$ , d,  $J_{4,5}$  7.5,  $J_{4,6}$  2.5 Hz), and 7.60 (2 H,  $\text{H}^{5,6}$ , m) p.p.m. due to the co-ordinated benzothiazole, and signals at  $\delta$  4.25 (4 H), 2.52 (4 H), and 1.87 (4 H) p.p.m. attributed to the co-ordinated cyclo-



SCHEME (i)  $-\text{H}^+$ ; (ii)  $+\text{D}^+$ ; (iii)  $+\text{CD}_3\text{OD}$ ,  $-\text{D}^+$ ; (iv)  $\text{MeOH}$  or  $\text{H}^+$  and  $\text{H}_2\text{O}$

such as alcohols, enhances the positive charge at  $\text{C}^2$  of the co-ordinated benzothiazole system and makes possible nucleophilic attack by the poor nucleophile  $\text{MeOH}$ . If interaction of the alcohol with the metal centre had been the favoured process, the positive charge induced at  $\text{C}^2$  would have been decreased and the ring-opening reaction hindered. Moreover, silver(I) stabilizes the open imidatoform making the  $\text{C-S}$  cleavage reaction irreversible.

In order to obtain further support for these ideas we have investigated the behaviour of benzothiazole derivatives co-ordinated to  $d^6$  (namely  $\text{Fe}^{\text{II}}$ ) and to  $d^8$  ( $\text{Rh}^{\text{I}}$ ) metal ions.

**Reactions of Iron(II) and Rhodium(I) Complexes.**—The complexes  $[\text{Fe}(\text{bt})_2\text{Cl}_2]$  and  $[\text{Fe}(\text{nbt})_2\text{Cl}_2]$  are thought to be six-co-ordinate in the solid state due to chlorine bridges among iron atoms. The u.v.-visible spectra in solution suggest that they retain this co-ordination number, at least in weakly co-ordinating solvents. It is conceivable, however, that the chlorine bridges will be split by co-ordinating solvents or other ligands.

We find that when solid  $[\text{Fe}(\text{nbt})_2\text{Cl}_2]$  is treated with methanol a white crystalline solid separates which is shown to be pure 6-nitrobenzothiazole. From the alcohol solution evaporated to dryness,  $\text{FeCl}_2 \cdot 6\text{CH}_3\text{OH}$  is recovered. Therefore, methanol displaces the ligand nbt or bt, and when the complexes  $[\text{FeL}_2\text{Cl}_2]$  ( $\text{L} = \text{bt}$  or

octadiene. These values are very close to those found for the rhodium(I) complex dissolved in  $\text{CDCl}_3$  alone, and show that no reaction takes place at room temperature. Moreover, no reaction takes place even when the sealed n.m.r. tube is heated for several hours at  $80^\circ\text{C}$ . On the other hand, when the  $\text{Rh}^{\text{I}}\text{-bt}$  complex is dissolved in deuteriated dmsO, the  $^1\text{H}$  n.m.r. spectrum changes to that of the free ligand bt (a singlet at  $\delta$  9.46 and two multiplets at 8.20 and 7.56 p.p.m. of relative intensities 1 : 2 : 2) and of the complex  $[\{\text{Rh}(\text{C}_8\text{H}_{12})\text{Cl}\}_2]$  (resonances at  $\delta$  4.43, 2.32, and 1.95 p.p.m. of relative intensities 4 : 4 : 4). These figures confirm that the benzothiazole is easily displaced in this complex, as previously observed.<sup>2</sup> Heating at  $100^\circ\text{C}$  for 3 h does not cause any evident reaction ( $\text{H-D}$  exchange or nucleophilic attack to benzothiazole or to the cyclo-octadiene).

#### EXPERIMENTAL

Infrared spectra were recorded on a Perkin-Elmer 577 spectrophotometer, and u.v.-visible spectra with a Zeiss apparatus. Hydrogen-1 n.m.r. spectra were recorded on a Varian 60 (or HA 100) spectrometer. The solvents were dried and distilled under nitrogen before use. All reactions were carried out in an atmosphere of pure nitrogen.

The compounds  $[\text{H}_6]\text{dmsO}$ ,  $\text{CD}_3\text{OD}$ , and  $\text{CH}_3\text{OD}$  were from Stohler Isotope Chemicals. 2-Methyl-6-nitrobenzothiazole and  $\text{Ag}[\text{ClO}_4]$  were crystallized before use.

*Preparations.*—The complexes  $[\text{Ag}(\text{bt})_2]\text{X}$  ( $\text{X} = \text{ClO}_4$  or  $\text{NO}_3$ ) and  $[\text{Rh}(\text{bt})(\text{C}_8\text{H}_{12})\text{Cl}]$  were prepared as reported elsewhere.<sup>1,2</sup>

*Bis(2-methyl-6-nitrobenzothiazole)silver(I) perchlorate*,  $[\text{Ag}(\text{mnbt})_2][\text{ClO}_4]$ . To a solution of mnbt (0.400 g, 2.1 mmol) in toluene (20 cm<sup>3</sup>) was added dropwise a solution of  $\text{Ag}[\text{ClO}_4]$  (0.200 g, 0.97 mmol) in toluene (50 cm<sup>3</sup>) at room temperature with stirring. A white crystalline complex precipitated which was filtered off, washed with water and pentane, and dried *in vacuo*. The complex is soluble in dimethylformamide and dimethyl sulphoxide. Yield: 0.560 g, 96%.

*(2-Methyl-6-nitrobenzothiazole)nitrat silver(I)*,  $[\text{Ag}(\text{mnbt})(\text{NO}_3)]$ . This complex was obtained from  $\text{Ag}[\text{NO}_3]$  (0.340 g, 2 mmol) dissolved in water-ethanol and the ligand mnbt (0.400 g, 2.1 mmol) dissolved in ethanol (10 cm<sup>3</sup>). The white complex precipitated was washed with water and cold ethanol, and dried *in vacuo*. Yield: 0.650 g, 90%.

*Dichlorobis(6-nitrobenzothiazole)iron(II)*,  $[\{\text{Fe}(\text{nbt})_2\text{Cl}_2\}_n]$ . To a solution of  $\text{FeCl}_2 \cdot 1.5 \text{ thf}$  (thf = tetrahydrofuran)<sup>12</sup> (0.86 g, 3.8 mmol) in thf (50 cm<sup>3</sup>) was added dropwise a solution of nbt (1.40 g, 7.7 mmol) in thf (20 cm<sup>3</sup>). A pale yellow solid precipitated which was filtered off, washed with cold thf and toluene, and dried *in vacuo*. Yield: 2.4 g, 93%.

The complex  $[\text{Fe}(\text{bt})_2\text{Cl}_2]$  was similarly obtained from the ligand and  $\text{FeCl}_2 \cdot 1.5 \text{ thf}$  in thf.

*Reactions with Alcohol.*—The complex to be studied was dissolved in  $[\text{D}_2\text{H}_8]\text{dmsO}$  under nitrogen in a n.m.r. tube and the spectrum was recorded. After addition of the appropriate alcohol ( $\text{CD}_3\text{OD}$  or  $\text{CH}_3\text{OD}$ ) the tube was sealed under nitrogen and the spectrum recorded at intervals of time.

This reaction was also carried out on a preparative scale under the same conditions.

*Characterization of the Ring-opened Products.*—(2-Amino-5-nitrobenzenethiolato)silver(I),  $[\text{Ag}\{\text{S}-\text{C}_6\text{H}_3(\text{NH}_2)(\text{NO}_2)\}] \cdot \text{dmsO}$ . The yellow-orange product deposited in the n.m.r. tube in one of the trials was filtered off, washed with benzene and

pentane, and dried *in vacuo* for 2 days at 25 °C. The i.r. spectrum in Nujol mull was identical to that of an authentic sample of (2-amino-5-nitrobenzenethiolato)silver(I) except for two bands at 1 045 and 1 020 cm<sup>-1</sup> due to the dmsO of crystallization.

(2-Aminobenzenethiolato)silver(I),  $[\text{Ag}\{\text{S}-\text{C}_6\text{H}_4(\text{NH}_2)\}]$ . The  $[\text{Ag}(\text{bt})][\text{NO}_3]$  complex was suspended in dry methanol and the suspension was shaken vigorously for several hours. The yellow product formed was washed with water, methanol, and pentane, and dried *in vacuo*. The i.r. spectrum in Nujol was identical to that of an authentic sample prepared from 2-aminobenzenethiol and silver nitrate in water-ethanol.

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