

SILVER(I) COMPLEXES OF 2-THIAZOLAMINE AND 2-BENZOTHAZOLAMINES

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Complexes of Silver(I) with 2-thiazolamine, 2-benzothiazolamine, 4-,5-,6-methoxy and 6-ethoxy-2-benzothiazolamine have been synthesised and characterised on the basis of physico-chemical data. The composition of the complexes in all these cases has been observed to be AgL_2NO_3 . The spectral data indicate that the ligands are coordinated to the metal atom via amino nitrogen. Electrical conductivity data in DMF suggest the complexes to behave as 1:1 electrolyte.

INTRODUCTION

Thiazole has two possible donor sites, sulphur and nitrogen. Substitution of an amino group at 2-position in the ring system provides an additional donor site and it may also behave as a tridentate chelate. The compound can also exist in the tautomeric imino form and act as an anionic ligand. Coordination behaviour of simple and substituted thiazoles and benzothiazoles with several first row transition metal ions has been studied and majority of the complexes are observed to be nitrogen bonded¹⁻⁵, however only few studies of their complexes have been reported with the second and third row transition elements⁶⁻⁸. Silver(I) ion has been characterized as a class B or 'soft' acid on the basis of reactivity and stability of its coordination complexes⁹.

Dash and Rao have reported 2-benzothiazolamine to be coordinated to the silver(I) ion through the ring sulphur atom¹⁰. In a number of complexes, 6-chloro and 6-methyl-2-benzothiazolamine have also been shown to be sulphur bonded^{11,12} while the corresponding 4- and 5-substituted 2-benzothiazolamine^{13,14} and 2-benzothiazolamine show the usual ring nitrogen linkage.

It is thus seen that the nature and position of the substituents in 2-benzothiazolamine affects the mode of coordination. We have, therefore, investigated a number of silver(I) complexes with 2-thiazolamine and 2-benzothiazolamine and their mode of linkage. For completeness, the complexes with the unsubstituted 2-thiazolamine and 2-benzothiazolamine have also been included.

EXPERIMENTAL

4-Methoxy-, 5-methoxy- and 6-ethoxy-2-benzothiazolamine were locally prepared from *o*-anisidine, *m*-anisidine and *p*-phenitidine respectively¹⁵. 2-Benzothiazolamine and 6-methoxy-2-benzothiazolamine of Koch-light were used as such. 2-Thiazolamine, Riedel, was recrystallised from benzene. Silver nitrate of E. Merck was used as such.

Preparation of the complexes

The concentrated solution of silver nitrate (1 mmol) in dry ethanol was treated with the ligands (2 mmol) also dissolved in small amounts of dry ethanol. White complexes, thus formed, were filtered, washed with dry ethanol and dried under IR lamp. Yield 40-86%.

The complexes are soluble in methyl cyanide and dimethyl- formamide, slightly soluble in methanol, ethanol and acetone but insoluble in other common organic solvents.

RESULTS AND DISCUSSION

The analytical data show that the isolated complexes have the general composition $[Ag(L_3)](NO_3)$. The molar conductivity values in DMF (105-151.5 $ohm^{-1} cm^2 mole^{-1}$) indicate the complexes to behave as 1:1 electrolyte.

The infrared bands are recorded in Table 1. The ligands exhibit strong to medium intensity bands in 3425-3365 cm^{-1} and 3315-3270 cm^{-1} region assigned as asymmetric and symmetric N-H modes respectively, which suffer an appreciable decrease in frequency as well as in intensity on complexation. δ_{NH_2} of the ligands are observed in 1648-1620 cm^{-1} region, which generally exhibit a positive shift from 5 cm^{-1} to 30 cm^{-1} in the complexes. Our observation regarding the behaviour of ν_{NH_2} bands are quite different from those of Dash and Rao¹⁰, they observed no change in ν_{N-H} of 2-benzothiazolamine at 3350 cm^{-1} in the silver(I) complexes whereas in the 2-benzothiazolamine complex of silver(I) prepared by us in dry ethanol exhibits a decrease of 100 cm^{-1} and 125 cm^{-1} in the asymmetric and symmetric N-H modes respectively. We have also prepared silver(I) complex of 2-benzothiazolamine in aqueous medium according to the method given by Dash and Rao¹⁰ and observed that the IR spectrum of this compound is completely superimposable on the IR spectrum of the complex prepared by us in dry ethanol and the report of the above authors stating that there is no shift observed in the ν_{N-H} region is thus not corroborated by our observation. It is generally observed that coordination through amino group involves a negative shift in ν_{NH_2} and a positive shift in δ_{NH_2} bands¹⁶, therefore bonding through the amino nitrogen is very likely in these complexes. The ν_{C-N} of the ligands in 1550-1515 cm^{-1} region generally shows an increase in frequency from 5 cm^{-1} to 27 cm^{-1} indicating the non-participation of ring nitrogen in coordination. The ν_{C-S} , which is observed in 640-595 cm^{-1} region in these ligands, shows a decrease in frequency in some of these complexes, which may probably be due to intermolecular interactions between the ring sulphur and the silver ion in the crystals. In all the complexes, new bands are observed in 283-265 cm^{-1} region, which are assigned as ν_{Ag-N} (amino). In most cases, the molar conductivity values in dimethylformamide are in the range expected for 1 : 1 electrolyte, which means that the nitrate group is outside the coordination sphere. Nitrate ion in potassium nitrate exhibits a sharp and medium intensity band¹⁷ at 817 cm^{-1} . For silver nitrate, we observe a similar band at 800 cm^{-1} which also appears in all the complexes around 800 cm^{-1} indicating the presence of ionic nitrate in the complexes. Considering the stoichiometry of the compounds and the coordination of two molecules of thiazolamines, we tentatively propose the linear geometry for the complexes.

TABLE 1
 PRINCIPAL IR BANDS (Cm^{-1}) OF SILVER(I) COMPLEXES AND LIGANDS

Band assignment	6OEt-2ABT	Ag(6OEt-2ABT) ₂ NO ₃	2ABT	Ag(2ABT) ₂ NO ₃
$\nu\text{NH}_2(\text{asym})$	3400s,msp	3310ms,mbr	3400ms,mbr	3300m,mbr 3390sh
$\nu\text{NH}_2(\text{sym})$	3270ms,msp	3160ms,mbr	3275ms,mbr	3150m,br
δNH_2	1622m,br 1630sh	1628ms,msp	1640s,sp 1630sh	1645s,mbr
$\nu\text{C}=\text{N}$	1528ms,mbr	1555s,sp 540sh 1570sp	1528s,msp	1555s,sp
$\nu\text{C}-\text{S}$	635ms,msp	628-600w,br	628ms,mbr	570-550vw,br
$\nu_{\text{Ag}-\text{N}}(\text{amine})$	—	283m,mbr	—	270w,mbr
Band assignment	2AT	Ag(2AT) ₂ NO ₃	6OMe-2ABT	Ag(6 OMe-2ABT) ₂ NO ₃
$\nu\text{NH}_2(\text{asym})$	3408ms,msp	3385, 3305 ¹ s,split	3390s,sp	3300s,msp
$\nu\text{NH}_2(\text{sym})$	3280s,br 3120-3080s,br	3210ms,msp 3140m,sp	3300ms,mbr	3300s,msp
δNH_2	1620s,mbr	1628s,sp	1605s,sp	1635s,sp 1640sh
$\nu\text{C}=\text{N}$	1515s,mbr	1538s,sp 1528sh	1550vs,vsp	1555s,sp 1540sh
$\nu\text{C}-\text{S}$	640m,mbr	628m,sp	615s,msp	620, 650 ¹ w,split
$\nu_{\text{Ag}-\text{N}}(\text{amine})$	—	265w,msp	—	275vw,br
Band assignment	5 OMe-2ABT	Ag(5 OMe-2ABT) ₂ NO ₃	4:OMe-2ABT	Ag(4 OMe-2ABT) ₂ NO ₃
$\nu\text{NH}_2(\text{asym})$	3365vs,sp	3370ms,msp	3425s,sp	3280mw,msp
$\nu\text{NH}_2(\text{sym})$	3315ms,sp	3300w,mbr	3280s,sp	3140ms,sl.br 3120sh
δNH_2	1648ms,sp	1650ms,msp	1620vs,sp	1620ms,sp
$\nu\text{C}=\text{N}$	1535vs,sp 1542sh	1550ms,msp 1530sh	1538ms,sp 1530sh	1540s,msp
$\nu\text{C}-\text{S}$	600w,msp	620ms,sl.br	595m,mbr	605m,sp
$\nu_{\text{Ag}-\text{N}}(\text{amine})$	—	275vw,br	—	275vw,br

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