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NOTE

Metal Complexes of 4- and 5-Methoxy-2-Benzothiazolamine

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Complexes of zinc(II), cadmium(II) and mercury(II) with 4-methoxy-2-benzothiazolamine (4-MeBT) and 5-methoxy-2-benzothiazolamine (5-MeBT), ML_2X_2 (M=Zn and X=Cl, Br, I; M=Cd and X=Cl, I L-4-MeBT or 5-MeBT), MLX_2 (M=Cd and X= Br; M=Hg and X=Cl, Br, I, L=4-MeBT or 5-MeBT) have been synthesized and characterised on the basis of physico-chemical data. The electrical conductivity values in DMF and acetone reveal their non-electrolytic nature in solution and the spectral evidence indicates that the ligands are coordinated to the metal atoms through the amino nitrogen.

The present paper describes the synthesis and characterization of zinc(II), cadmium(II) and mercury(II) complexes of 4-methoxy-2-benzothiazolamine (4-MeBT) and 5-methoxy-2-benzothiazolamine (5-MeBT).

$ZnCl_2$, $CdCl_2$ and HgI_2 of S.M. (LR); $CdBr_2$ of E. Merck; $HgCl_2$ and CdI_2 of BDH (A.R.) and ZnI_2 of Koch-Light were used as such. 4-Methoxy- and 5-methoxy-2-benzothiazolamine were prepared from *o*-anisidine and *m*-anisidine, respectively in the laboratory[1].

Preparation of the Complexes

ZnL_2X_2 (X=Cl, I), CdL_2X_2 (X=Cl, Br, I), $HgLX_2$ X(X=Cl, I): The solution of the metal halide (1 mmol) in dry methanol were treated with the methanolic solution of the ligand (2 mmol). The complexes thus formed were filtered and washed with dry methanol and ether and dried under IR lamp. However the iodo complexes were washed with methanol only.

ZnL_2Br_2 and $HgLBr_2$: An aqueous solution of KBr (2 mmol) was added to the methanolic solution of metal chlorides (1 mmol) and evaporated to dryness; the residues were extracted with methanol to remove KCl and treated with the ligand (2 mmol) dissolved in methanol, the complexes were filtered off and washed with methanol and ether and dried under IR lamp.

The elemental analyses of the complexes indicate the general composition ML_2X_2 (M=Zn and X=Cl, Br, I; M=Cd and X=Cl, I; L=4-MeBT or 5-MeBT); MLX_2 (M=Cd, and X=Br, M=Hg and X=Cl, Br, I, L=4 MeBT or 5 MeBT). The electrical conductivity values in DMF and acetone reveal their non-electrolytic nature in solution.

2-Aminobenzothiazole exhibits a medium intensity $\nu_{NH_2(asym)}$ and $\nu_{NH_2(sym)}$ bands at 3400 cm^{-1} and 3275 cm^{-1} respectively in the solid state[2,3]. Substituted 2-benzothiazolamines *e.g.* 6-Ethoxy-, 6-methoxy-, 5-methoxy- and 4-methoxy-2-benzothiazolamine also show these bands in 3425–3365 cm^{-1} and 3315–3280 cm^{-1} region[1,4]. In benzene solution both asymmetric and symmetric N–H modes show an increase of 125–45 cm^{-1} and 110–70 cm^{-1} respectively. The IR spectra of all these ligands were also taken in acetone and it was observed that the positive shifts of $\nu_{NH_2(asym)}$ and $\nu_{NH_2(sym)}$ are less as compared to solution in benzene. The increase of these modes in benzene indicates the presence of intermolecular hydrogen bonding in the solid state[5]. From the structure of the ligand it appears that there is a possibility of intermolecular hydrogen bonding between the $-NH_2$ groups or between the $-NH_2$ and alkoxy groups. The δ_{NH_2} and $\nu_{C=N}$ modes of the ligands in solid state were observed in 1640–1620 cm^{-1} and 1535–1530 cm^{-1} region respectively as strong intensity bands[2,6,7]. The $\nu_{C=N}$ bands remain unaffected in solution whereas the deformation N–H modes suffered a negative shift in the solution. The observed decrease of δ_{NH_2} in acetone is again suggestive of hydrogen bonding in the solids[5]. All these ligands also show a broad and medium intensity band in 600 cm^{-1} region assigned to ν_{C-S}[8,9].

On comparing the spectra of the complexes with the ligands in acetone, we observe that the asymmetric and symmetric N–H modes exhibit an appreciable decrease in frequency as well as in intensity; also in some of these complexes these are observed to get split. It indicates the involvement of amino group in coordination. The $\nu_{C=N}$ remains unaffected and appears as a strong band in 1530 cm^{-1} region in all the complexes; therefore, coordination through ring nitrogen is less likely. The ν_{C-S} of the ligands suffers a positive shift of about 40 cm^{-1} in these complexes. It is generally observed that ν_{C-S} shows a shift to lower region when the ring sulphur is involved in coordination[10–12], hence bonding through the sulphur atom is also less likely in these complexes. Therefore, we propose the linkage of the ligands through the amino group in all these complexes. A medium intensity band is observed in 330–280 cm^{-1} region in the complexes which is due to ν_{M-N}.

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