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NOTE

Binuclear Complexes of Class A Metals with *o*-Hydroxy-bis-Benzene-azo-Resorcinol

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A series of bi-nuclear mixed ligand complexes of class A metal salts of different organic acids with *o*-hydroxy-bis-bezene-azo-resorcinol have been synthesised of the general formula $(ML)_2$-OH-BAR, where M = Na and K; L = deprotonated organic acids; 1-nitroso-2-naphthol, 8-hydroxy quinoline, *o*-nitro-phenol, 2-hydroxy-3-naphthoic acid, anthranilic acid and OH-BAR = *o*-hydroxy-bis-benzene-azo-resorcinol. On the basis of analytical results and IR spectra these complexes have been characterised.

In our earlier works[1, 2] we have reported the formation of alkali-metal complexes with azo-ligands containing electron pushing groups as well as electron withdrawing groups at *o* and *o'*-positions to the azo-group. Recently synthesis and spectral characterisation of high yield tetra-coordinated bis-N(I)-alkyl-2-(aryl azo) imidazole silver(I) complexes have been reported[3]. To cultivate the field of alkali-metal complexes, we have selected this work in which we are reporting the alkali-metal complexes formed with this interesting ligand *o*-hydroxy-bis-benzene-azo-resorcinol which contains (—N=N—) groups as well as OH-groups at *o*- and *o'*-position. The complexes of general formula $(ML)_2$-OH-BAR have been synthesised, where M = Na and K, L = deprotonated organic acids, 1-nitroso-2-naphthol, 8-hydroxy quinoline, *o*-nitrophenol, 2-hydroxy-3-naphthoic acid and anthranilic acid and OH-BAR = *o*-hydroxy-bis-benzene-azo-resorcinol. The structure assessment and the stability of the complexes in non-aqueous solvent, *e.g.*, ethanol have been made on the basis of analytical results and IR spectra.

The complexes are stable when stored under dry condition. All the complexes are coloured. When heated, they undergo a decomposition at a temperature much higher than the melting point of ligand. The colour and decomposition temperatures are given in Table-1.

In the ligand OH-BAR, we obtained the azo band (—N=N—) at 1530 cm^{-1}. In the complexes this band shifts down to 1510–1500 cm^{-1} suggesting that the —N=N— group is coordinated to the metal. These bands also split in the

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complexes, due to change in the symmetry. The —N=N— frequency of ligand OH-BAR and its complexes with alkali metal salts have been given in Table-1.

TABLE-1
PHYSICAL PROPERTIES AND IR BAND (cm^{-1}) OF THE COMPLEXES

Compounds	Colour	Decomposition temp. (°C)	—N=N—
OH-BAR = L	Reddish violet	255	1530
(Na 1N2N)$_2$L	Deep reddish violet	275	1500, 1510
(K 1N2N)$_2$L	Deep reddish violet	280	1505, 1510
(Na 8HQ)$_2$L	Brown	285	1510
(K 8HQ)$_2$L	Brown	290	1505
(Na ONP)$_2$L	Dark brown	270	1500
(K ONP)$_2$L	Dark brown	275	1500
(Na 2H3NA)$_2$L	Dark brown	285	1505
(K 2H3NA)$_2$L	Dark brown	285	1505
(Na anth)$_2$L	Brown	290	–
(K anth)$_2$L	Brown	295	–

OH-BAR = *o*-hydroxy-bis-benzene-azo-resorcinol;
1N2N = 1-nitroso-2-naphthol,
8HQ = 8-hydroxy quinoline; ONP = *o*-nitrophenol;
2H3NA = 2-hydroxy-3-naphthoic acid; anth = anthranilic acid

The —OH stretching frequency of the ligand has been observed at 3300 cm^{-1}. In $(ML)_2$ OH-BAR complxes it shifts down to 3200 cm^{-1}. It shows the involvement of —OH in the formation of complexes. The potassium complexes seem to be more stable and strong than their corresponding sodium analogues.

The ligand OH-BAR was prepared by standard method.[4] Its melting point was 255°C and all the alkali metal salts used were prepared in 95% ethanol.

General Methods of Preparation of Complexes

To the hot absolute ethanolic solution of OH-BAR, the alkali-metal salts of organic acids was added in 1 : 2 molar ratio. The whole mixture in solution was refluxed over water bath and stirred for about more than 1 h. The solution on keeping yielded crystalline solid compounds. The crystals were filtered, washed with absolute alcohol and dried in an oven at 80°C.

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